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Theoretical study of the mechanism of 2,5-diketopiperazine formation during pyrolysis of proline

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DEDICATORIA

El presente trabajo lo dedico afectuosamente a mi esposa y a mi madre, cuyo apoyo durante estos dos años de estudios fueron primordiales para cumplir con este reto.

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Theoretical study of the mechanism of 2,5-diketopiperazine formation during pyrolysis of proline

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ABSTRACT

The mechanism of formation of 2,5-diketopiperazine upon pyrolysis of proline at 300ºC was theoretically studied by means of DFT calculations (wB97XD/6-311g(d,p)). All transition states and minimum energy structures involved were optimized, and thermodynamic parameters were theoretically estimated. The reaction occurs through a mechanism of four steps where the second one, which consists in a dehydration process, contains the highest activation enthalpy. The latter step was analyzed by using the reaction force formalism, and an analysis of geometrical parameters, charge distributions and bond orders. The results show that the first intermediate (INT1) and its subsequent transition state (TS2) are the most important rate-controlling states. The energetic barrier is formed by a 75% of geometrical rearrangements while the proton transfer needed to form water and achieve the dehydration represents the remaining 25%. INT1 appears to be a very stable intermediate due to the high dominancy of geometrical rearrangements for both, the forward and the reverse reaction. Changes of less than ±0.1 in the charges of atoms demonstrate that charge transfer is not an important factor for the analyzed reaction step. Finally, from the bond order analysis, it is determined that TS2 is an early transition state, and that the process is asynchronous.

1. INTRODUCTION

The pyrolysis of organic compounds is an important process in which a substrate thermally decomposes upon exposure to temperatures above 200ºC. It involves changes in the chemical composition of a molecule that are irreversible, giving rise to stable products. Reactions based-on elimination mechanisms have been proposed as the main pathways during pyrolysis [1]. Therefore, this particular idea has been extensively explored, by theoretical and experimental means, for simple organic compounds such as: carboxylic acid derivatives [2,3], alkyl halides [4], ketals [5], and amino acids [6–8]. In the particular case of the latter, their pyrolysis has been subject of intensive study due to the increasing interest in the thermal decomposition of biomass at high temperature [6]. Furthermore, it is important to point out that the biomass combustion leads to the production of environmentally harmful nitrogen containing polycyclic compounds [9,10] which differ in their identity and yield, depending on the temperature of the process, the residence time, and the chemical structure of the specific amino acids that are present in the protein composition of the biomass sample [11].

The pyrolysis of amino acids form products based on reactions of dehydration, decarboxylation, or deamination, leading to common volatiles such as H_2O, NH_3, CO_2, CO, HNCO, y HCN [7,12]. However, formation of higher molecular weight products like 2,5-diketopiperazine (DKPs) compounds [7,11], maleimide. succinimide, glutaramide, pirrolidone, and others [7,10] have been also observed as products during pyrolysis of these substrates. It has to be indicated that the formation of high molecular weight products from the pyrolysis of small organic compounds is not common in literature due to the decomposition nature of pyrolysis, which commonly imply an elimination reaction as commented before. Thus, the pyrolysis of amino acids represents a special case on these regards. Among the amino acids for which the formation of DKPs has

been reported, proline shows the highest production after pyrolysis at 300ºC, resulting in a yield ca. 80% of the corresponding DKP [8,13]. It is important to remark that, when pyrolysis is carried out for extended times, even the DKP is decomposed to form the aforementioned common volatile products [14]. In this sense, during the pyrolysis of proline, the final possible formation of ammonia and hydrogen cyanide, which are potentially toxic for human beings, has attracted the interest of the scientific community considering that this amino acid is commonly found in cigarettes [15].

Previous theoretical studies of the proline pyrolysis mechanism have been centered on its unimolecular decomposition [16]. Results obtained at the B3LYP/6-311g(2d,p) level of theory suggested that dehydration and decarboxylation reactions are the dominant unimolecular processes at a wide range of temperatures and pressures [16]. However, the formation of DKP during the pyrolysis of proline at 300°C, has not been explored although the experimental results obtained from gas chromatography/mass spectrometry suggests its formation through a dimerization of proline [8]. The objective of this work is to theoretically study the reaction mechanism for 2,5-diketopiperazine formation during the pyrolysis of proline at 300°C [17] and determine whether the formation of DKP is more favorable or not over the unimolecular decomposition.

2. COMPUTATIONAL METHODOLOGY

All the calculations were performed using the Gaussian 16 suit of programs [18]. Geometry optimizations for all stationary points along the proposed mechanism (reactive, product, intermediates, and transition states) were calculated at DFT level of theory, using the wB97XD functional [19], and the 6-311g(d,p) basis set [20,21]. For the appropriate description of the transition state geometries, where differences of electronegativity and charge transfer could be important, a long-range dispersion-corrected functional was employed which has satisfactory accuracy for non-covalent

and non-bonded interactions[19], while the selected basis set with polarization functions ensures to accurately describe the electronic configuration [21]. Frequency calculations at 300ºC were performed on the optimized molecules at the same level of theory, ensuring the existence of a unique imaginary eigenvalue in the Hessian matrix for transition states, and no imaginary eigenvalues for minimum energy configurations. The correlation of the corresponding transition vectors to the reaction pathway were also verified.

In order to analyze the thermodynamic properties of the mechanism, values of absolute enthalpies (H) were collected from the frequency output files from DFT calculations, while absolute Gibbs free energies were obtained using the Goodvibes v 2.0.3 program [22] which applies the quasi-harmonic approximation to the vibrational entropy and leads to quasi-harmonic corrected Gibbs free energies. The program was used by setting the temperature at 573.15 K, the approach proposed by Grimme in Ref. [23], and the rest of parameters as default.

Degrees of rate control (X_{RC}) for all involved transition states were calculated according to the procedure described by Motagamwala [24] (See Supplementary Information for details). Equation (1) is used to calculate the degree of rate control of the *i-th* transition state on a generalized sequence of n steps:

$$X_{RC,i} = \frac{\prod_{j=1,j\neq i}^{n} r_{max,j}}{\sum_{j=k}^{n}\left(\prod_{j=1,j\neq k}^{n} r_{max,j}\right)} \qquad (1)$$

Where $r_{max,i}$ is called the maximum rate of the *i-th* step, and is obtained according to equation (2):

$$r_{max,i} = \frac{k_B T}{h} K^{\dagger}_{eq,A\rightarrow TS_i}[CF] \qquad (2)$$

Here, $K^{\dagger}_{eq,A\rightarrow TS_i}$ is a condensed constant which contains a combination of rate constants (k_j) and equilibrium constants ($K_{eq,j}$) of any elemental step involved in the

reaction pathway from the reactive to a *i-th* transition state. [CF] is a "concentration factor" which contains a combination of molar concentrations (or partial pressures in gas-phase reactions) of any reactive, product or by-product involved in the process. Neither $K^{\dagger}_{eq,A\rightarrow TS_i}$ nor [CF] have a general expression, and they have to be obtained for each particular case (check the Supplementary Information). k_B and h are the Boltzman's and Plank's constants, respectively, and T is the temperature of the process.

Additionally, the evolution of the DFT energy along the normalized reaction coordinate (ξ) between each stationary point was determined by Intrinsic Reaction Coordinate (IRC) calculations, and the profiles resulting for the rate controlling step were selected to a further detailed analysis by means of the reaction force formalism.

Reaction force ($F(\xi)$) profiles [25,26] were obtained numerically, according to equation (3):

$$F(\xi) = -\frac{dE}{d\xi} \qquad (3)$$

By identifying the points on the reaction coordinates where critical points exist ($F(\xi) = 0$), and the maximum and minimum of the reaction force, the reaction path can be divided in regions (j) in which geometrical and electronic rearrangements are dominant on each step (i) of interest. Upon region determination, values for works ($w_j^{(i)}$) are numerically calculated, from critical point *a* to critical point *b*, according to equation (4).

$$w_j^{(i)} = -\int_a^b F(\xi)d\xi \qquad (4)$$

In order to obtain more detailed information about the mechanism, data of some selected geometrical parameters over the reaction coordinate were extracted from the IRC calculation outputs, which contain all the geometrical coordinates of atoms in each of the points plotting the IRC profile.

A Natural Bond Orbital (NBO) calculation [27] was also performed to gain additional insights on the process. Data associated to the charge on some selected atoms were extracted from NBO outputs of each of the corresponding stationary points involved in the determining reaction step. Subsequently, changes in the electronic distribution of each atom were quantified as a difference of charge, calculated for each of the atoms involved in the process, with equation (5).

$$\delta Q_{X\to Y}^{atom} = Q_Y^{atom} - Q_X^{atom} \qquad (5)$$

Where $\delta Q_{X\to Y}^{atom}$ (or δQ for simplicity) is the difference of charge between stationary point X to stationary point Y, while Q_X^{atom} and Q_Y^{atom} are the NBO charge in each corresponding stationary point.

Similarly, from the corresponding NBO outputs, changes in Wiberg bond indexes [28] were also analyzed to get more information. These changes were calculated as a fractional difference of bond order, using equation (6).

$$\delta B_{X\to Y}^{bond} = \frac{B_Y^{bond} - B_X^{bond}}{B_Z^{bond} - B_X^{bond}} \qquad (6)$$

Where $\delta B_{X\to Y}^{bond}$ (or δB for simplicity) is the fractional difference of bond order between minimum X to the transition state Y, while B_X^{bond}, B_Y^{bond} and B_Z^{bond} are the Wiberg bond indexes in the corresponding stationary point: the minimum X, the transition state Y, and the following minimum Z.

Finally, the synchronicity [29] of the step of interest was computed by using equation (7).

$$Sy = 1 - \frac{\sum_{i=1}^{n} |\delta B_i - \delta B_{average}|}{\delta B_{average}\,(2n-2)} \qquad (7)$$

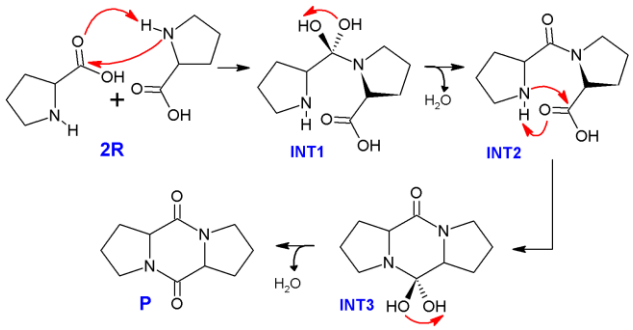
Where Sy is the synchronicity of a specific step, n is the number of bonds (only those bonds that change significantly are taken into account), δB_i is the fractional difference

of bond order for the i-esime bond, and $\delta B_{average}$ is the average of all δB_i taken into account.

3. RESULTS AND DISCUSSION

3.1.Mechanism of reaction and thermochemistry properties

Scheme 1 shows the mechanism for pyrolysis of proline studied in this work. This mechanism is based on the suggestion of Chiavari et al [8], who mentioned that after the proline dimerization (step 1), a double dehydration process (steps 2 and 4) and cyclization (step 3) lead to the DKP product (P).



Scheme 1. Reaction mechanism proposed for proline pyrolysis

Each stationary point (reactant, transition states, intermediates and product) was separately optimized, and the differences of enthalpy between each pair of points were calculated using the absolute thermochemical values obtained from DFT frequency calculations (see Table 1). With these data, a reaction profile based on normalized enthalpies is shown in Figure 1.

Table 1. Thermodynamic parameters calculated from absolute enthalpies and entropies obtained through the DFT calculation: wb97xd/6-311g(d,p)

i	X	Y	ΔH_i $H_Y^{DFT} - H_X^{DFT}$ (kJ mol^{-1})	Normalized Enthalpy H_Y (kJ mol^{-1})
--	--	2 R	---	0.0
1	2 R	TS1	129.2	129.2
-1	TS1	INT1	-145.2	-16.0
2	INT1	TS2	174.2	158.2
-2	TS2	INT2+H_2O	-153.8	4.4
3	INT2+H_2O	TS3	113.8	118.1
-3	TS3	INT3	-133.7	-15.6
4	INT3	TS4	108.2	92.7
-4	TS4	P+H_2O	-142.5	-49.9

Note: Temperature used for the DFT calculations was 573.15 K

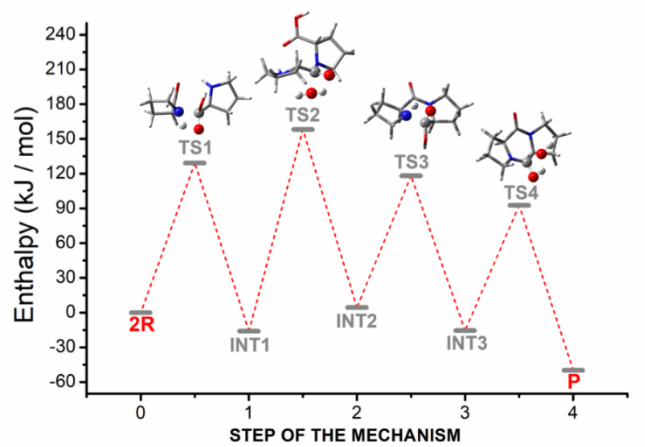


Figure 1. Enthalpy profile for the formation of 2,5-diketopiperazine product through a dimerization process. Structures of TS in the top of the figure are the optimized geometries.

Although INT1 and INT3 are more stable than the reactive (2R), all intermediates are unstable when compared with the product (P); therefore, the global reaction is exothermic ($\Delta H_{reaction}$= – 49.9 kJ/mol). Additionally, since the change in the Gibbs free energy for the global reaction is negative ($\Delta G_{reaction}$= – 110.9 kJ/mol), it can be stablished that the process is spontaneous.

From the differences of barriers of Figure 1, it can be assumed that the main processes of the reaction depends on the first two steps: the dimerization of proline, and the subsequent elimination of a molecule of water. After that, it appears that faster steps consisting in a less energy-demanding cyclization and a second elimination of water will finally form the 2,5-diketopiperazine product. In these regards, the details about the determination of the degree of rate control for this particular reaction mechanism are presented in the next section.

3.2.Determination of the degrees of rate control

In order to describe the kinetic properties of the proposed mechanism, the following reaction steps and rate constants are considered:

$$2R \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} INT1 \qquad (8)$$

$$INT1 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} INT2 + H_2O \qquad (9)$$

$$INT2 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} INT3 \qquad (10)$$

$$INT3 \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} P + H_2O \qquad (11)$$

Now, according to Motagamwala [24], the degrees of rate control (X_{RC}) for transition states can be calculated using equations (1) and (2) (See details in Supporting Information). Results are summarized in Table 2:

Table 2. Rate constants, equilibrium constants, maximum rates, and degrees of rate-control for elementary steps on the mechanism of formation of 2,5-diketopiperazine from pyrolysis of proline

i	$\boldsymbol{k_i}$ $\frac{k_B T}{h} e^{-\frac{\Delta G_i^{qh}}{RT}}$ (s^{-1})	$\boldsymbol{K_{eq,i}}$ k_i/k_{-1} (dimensionless)	**Expression for** $\boldsymbol{r_{max,i}}$	$\boldsymbol{r_{max,i}}$ eq.(2) (s^{-1})	$\boldsymbol{X_{RC,i}}$ eq.(1) (dimensionless)
1	1.10×10^{-10}	4.59×10^{-10}	$k_1[R]^2$	1.10×10^{-10}	4.14×10^{-3}
-1	2.39×10^{-1}	---	---	---	---
2	9.94×10^{-4}	9.81×10^{6}	$k_{eq,1}k_2[R]^2$	4.56×10^{-13}	9.96×10^{-1}
-2	1.01×10^{-10}	---	---	---	---
3	1.82×10^{1}	5.03×10^{0}	$k_{eq,1}k_{eq,2}k_3\,[R]^2[H_2O]^{-1}$	8.22×10^{-2}	5.53×10^{-12}
-3	3.63×10^{0}	---	---	---	---
4	1.83×10^{3}	5.19×10^{11}	$k_{eq,1}k_{eq,2}k_{eq,3}k_4[R]^2[H_2O]^{-1}$	4.14×10^{1}	1.10×10^{-14}
-4	3.53×10^{-9}	---	---	---	---

Note: For the determination of rate constants (k_i), quasi-harmonic corrected Gibbs free energies (ΔG_i^{qh}) were obtained by using the Goodvibes v 2.0.3 program. The temperature (T) used in calculations was 573.15 K. k_B and h are the Boltzman's and Plank's constants, respectively.

These degrees of rate control represent an indicator of how much influence has a transition state on the total reaction rate. The farther the $X_{RC,i}$ from zero the more significant the influence in the rate of the reaction is higher. The sum of all X_{RC} must be the unity.

From the calculated values, TS2 corresponds to the most influent transition state on the reaction rate with a $X_{RC,TS2} = 0.996$, while the rest of $X_{RC,i}$ are almost zero. Looking at the minimum configurations, INT1, which precedes TS2, represents the most stable intermediate in the profile. The energy barrier formed from INT1 to TS2 is the highest one. Therefore, the second elemental step of the mechanism, the dehydration process, can be suggested as the most important step on the rate of the process.

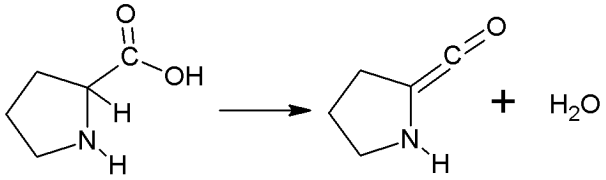
It is interesting to notice that the second dehydration (the fourth step), is not as important to the reaction rate as the first one. Considering that the molecule has lost a

rotational degree of freedom when it becomes a cycle, the second dehydration should be less geometrically demanding, and therefore, more favored than the first dehydration.

3.3.Determination of the overall activation energy

Although the first dehydration process (from INT1 to TS2) contains the rate determinant states of the mechanism as indicated in the last section, due to the fact that formation of INT1 is exothermic and contributes with approximately 16 kJ/mol to the reaction energy, the net energetic barrier should be corrected by subtracting this value to the activation energy of the dehydration; in other words, the net energy of the reaction should be considered as the difference of enthalpy from 2R to INT2. Whit the last consideration, it can be stablished that the global reaction needs to overcome an activation enthalpy ($\Delta H^{\ddagger}$) of 158.2 kJ/mol.

The dimerization mechanism presented in this work is compared with the unimolecular decomposition of this substrate, which was previously theoretically studied by Rawadieh et al [16]. According to Rawadieh, the unimolecular process during pyrolysis of proline involve a direct dehydration of this amino acid [16], as depicted in Scheme 2.



Scheme 2. Reaction for the most favored unimolecular process during proline pyrolysis, according to Rawadieh et al.

An activation enthalpy of 315.7 kJ/mol was calculated by us for this reaction at the wB97XD/6-311G(d,p) level, which is in agreement with the reported value of 297.1 kJ/mol (71.0 kcal/mol) obtained by Rawadieh at the B3LYP/6-311G(2d,p) level [16]. By comparing this barrier against the DKP formation (158.2 kJ/mol), it is possible to conclude that the dimerization is favored, with a requirement of approximately half of

the energy needed for the mentioned unimolecular reaction. This difference in activation barrier allows us to explain why the DKP product is the main compound in low temperature pyrolysis [8].

3.4. Electronic energy through the intrinsic reaction coordinate (IRC), reaction forces (RF), and works (w)

The electronic energy over the reaction coordinate from 2R to INT2 is studied. Specifically, the barriers governed by k_2 (INT1→TS2) and k_{-1} (INT1→TS1) are analyzed using the reaction force approach (see Figure 2). The involved works ($w_j^{(i)}$) were calculated by numerical integration of the area under the curve for each region (j) of each reaction step (i) in the reaction force plot.

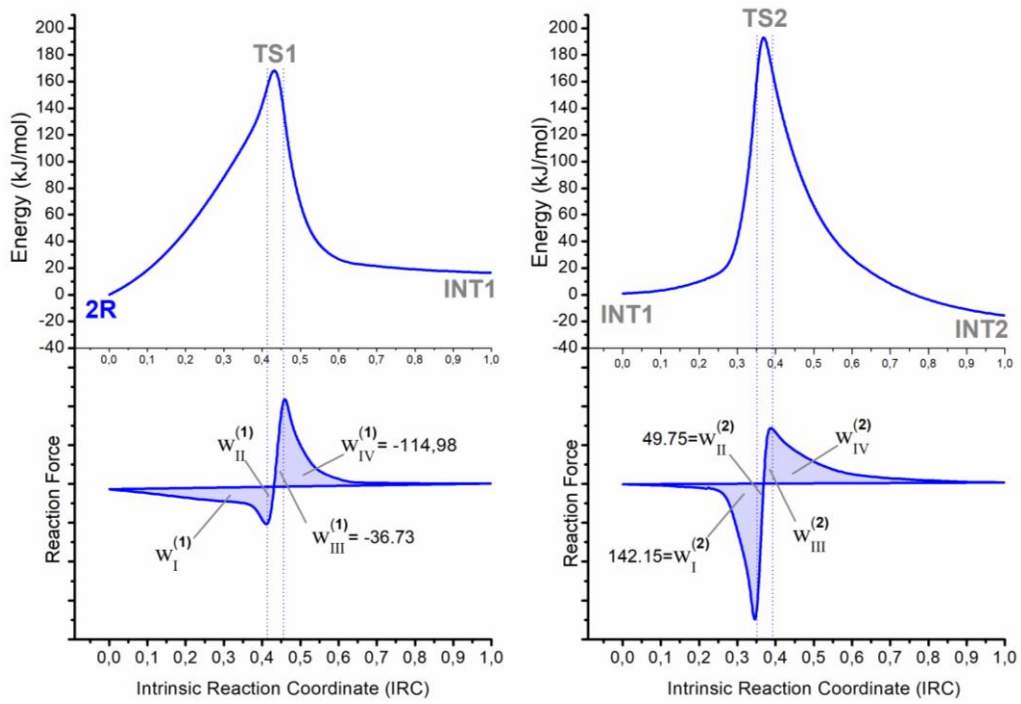


Figure 2. Total electronic energy through the reaction coordinate of the two elemental steps involved in the formation of the dipeptide of Proline: dimerization step (left) and dehydration step (right); and their corresponding Reaction Force plots (first derivative of the energy) and works (area under the curve). Work's values are in kJ/mol.

Due to the fact that absolute values of works corresponding to so-called geometrical interactions ($w_{IV}^{(1)}$ and $w_{I}^{(2)}$) are higher than those corresponding to electronic ones ($w_{III}^{(1)}$ and $w_{II}^{(2)}$), the conversion of INT1 to whether INT2 or 2R, is predominantly dominated by the geometry rearrangement of the molecule, which in both cases represent approximately 75% of the energy needed to overcome the barrier. It could be related to the fact that INT1 is the most influent intermediate to the rate of the reaction as mentioned earlier.

3.5.Geometrical parameters of INT1 through the reaction coordinate

For both, forward and reverse directions from INT1, the geometrical changes of the molecule are analyzed (see Figure 3).

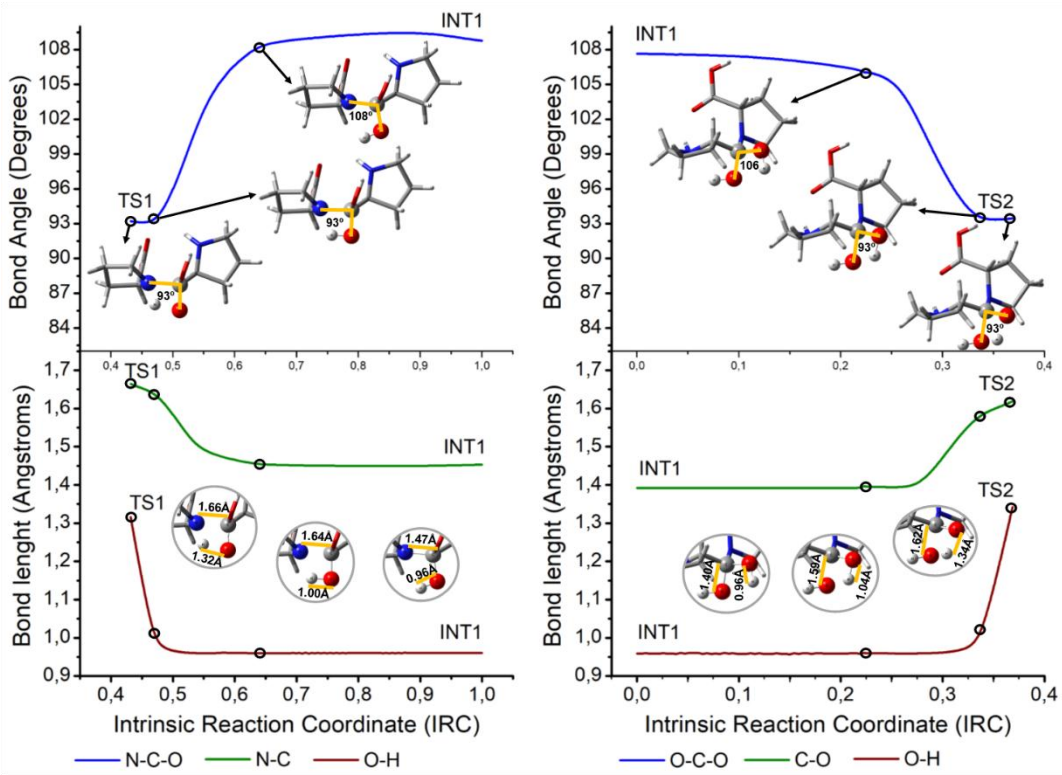


Figure 3. Change in the bond angle between atoms N–C–O from TS1 to INT1 (left), and between atoms O–C–O from INT1 to TS2 (right).

In order to achieve TS2 to dehydrate the dimer, INT1 requires the approximation of the alcohol groups in order to obtain an oxygen-to-oxygen proton transfer. This is

achieved by decreasing the O–C–O angle from 107º to 93º, and keeping this latter value during the proton transfer. C-O and O-H distances are practically kept constant upon completion of the proton transfer, then these bonds rapidly change from 1.40 to 1.62 Å, and from 0.96 to 1.34 Å, respectively. Notice that the C-O bond starts to break a few earlier than the O-H bond.

In the reverse path, the angle between the N–C–O in INT1 decreases from 109º to 93º in order to form the initial proline molecules; thus, the proton transfer (from oxygen to nitrogen), and the rupture of the dimer, can be achieved. Looking at the N-C and O-H distances, a similar behavior than in forward direction can be seen: the proton transfer occurs at the end changing O-H distance from 0.96 to 1.32 Å, while the N-O bond rupture starts a few earlier with a change from 1.47 to 1.66 Å.

3.6.Charge distribution and bond order changes from INT1 to TS2

TS2 is a transition state of four members (see Figure 4) where the oxygen atoms are rich in electronic density while the carbon and hydrogen atoms are deficient.

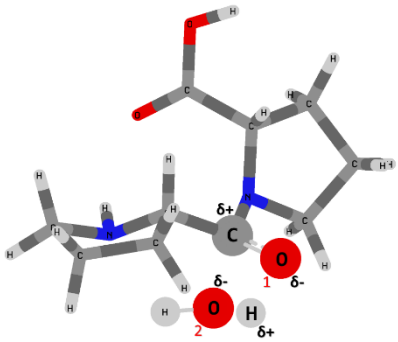


Figure 4. Optimized structure of TS2, showing the four atoms involved in the process of dehydration. Oxygen atoms have been labelled as O(1) and O(2) to differentiate them.

Focusing on the differences between TS2 and INT1, the changes in electronic distribution were quantified as a difference of charge ($\delta Q^{atom}_{INT1 \rightarrow TS2}$, or δQ for simplicity), calculated for each of the four atoms involved in the process, with the

equation (5). All values obtained for δQ (see Table 3) belongs on the range between -0.09 to 0.06; those relatively small values suggest that charge transfer is not an important parameter to achieve TS2, which is coherent with the reaction force analysis where geometric rearrangement is the most important factor.

Table 3. Electronic density for selected atoms and change in the charge

	O(1)	**H**	**O(2)**	**C**
INT1	-0.78	0.48	-0.78	0.77
TS2	-0.87	0.54	-0.80	0.80
$\boldsymbol{\partial Q^{atom}_{INT1\rightarrow T}}$	**-0.09**	**0.06**	**-0.03**	**0.02**

By analyzing the changes in Wiberg bond indexes of TS2 respect to INT1 (see Table 4), the fractional difference of bond order ($\delta B^{bond}_{INT1\rightarrow TS2}$, or δB for simplicity) was calculated using the equation (6). When a bond is broken or formed between two intermediates, δB represents a measure of how much that bond have been transformed when the reaction reached the corresponding transition state; a δB = 0 means that the bond has not changed during the process, while a δB = 1 means a complete bond conversion. Additionally, Table 4 shows: the average of all δB, which lets estimate if the transition state is an early TS ($\delta B_{average}$ < 0.5), or a late TS ($\delta B_{average}$ > 0.5); and the synchronicity of the step, as defined by equation (7), which represents how synchronous is the process.

Table 4. Wiberg bond indexes for selected bonds and change in the charge distribution

	O(1) – – H	**O(2) – – C**	**O(2) – – H**	**O(1) =–= C**	$\boldsymbol{\delta B_{average}}$	$\boldsymbol{Sy}$
INT1	0.752	0.943	0.003	0.897	-	-
TS2	0.262	0.626	0.422	1.160	-	-
INT2	0.005	0.006	0.778	1.646	-	-
$\boldsymbol{\partial B^{bond}_{INT1\rightarrow TS2}}$	**0.656** single- bond rupture	**0.339** single-bond rupture	**0.541** single-bond formation	**0.352** double-bond formation	**0.472**	**0.821**

Values of δB in Table 4 show that the O(1)–H rupture and the O(2)–H formation are the principal electronic rearrangements that occur to achieve TS2, while C–O(2) rupture and C=O(1) formation are mainly completed after the TS. This observation proves that, due to the known instability of hydroxyl anions, water molecule is mostly formed first, and then it is separated from the molecule matrix. Additionally, the $\delta B_{average}$= 0.472 means that TS2 is an early transition state, which corresponds well with the intrinsic coordinate (< 0.5) where TS2 is located (see Figure 2). Finally, the value for synchronicity (Sy = 0.821) express that the process is non synchronous, which represents a TS in a concerted slightly polar process.

4. CONCLUSIONS

The dominancy of the geometrical type rearrangements needed to achieve weather TS2 or TS1, along with the high activation energies in both ways, makes INT1 a very stable intermediate. However, since INT1 is more energetic than P, it keeps as an intermediate in the process. With these information, it can be understood the fact that the dehydration step, which contains both rate controlling states (INT1 and TS2), is the most influent step on the rate of the mechanism. Here, the geometrical rearrangements needed to achieve TS2 are dominated by the approximation of the oxygen atoms involved in the proton transfer, while electronic rearrangements depend on the almost formation of the molecule of water just before its separation from the molecular matrix. Electronic rearrangements do not need a significant charge transfer, possibly because the process is slightly asynchronous because rupture and formation of bonds occur almost at the same time.

ASSOCIATED CONTENT

Supporting Information

Additional information is available free of charge. This material contains: A) A detailed development for the determination of degrees of rate control; B) The optimized geometries of each transition state of the profile; C) DFT energy through the intrinsic reaction coordinate (IRC) for each step of the mechanism.

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SUPPORTING INFORMATION

A. Development of the determination of degrees of rate control

According to Motagamwala[1], degrees of rate control (X_{RC}) for transition states can be calculated by the following procedure:

Considering the following four-step reaction scheme:

(1) $2R \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} INT1$

(2) $INT1 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} INT2 + H_2O$

(3) $INT2 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} INT3$

(4) $INT3 \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} P + H_2O$

The reversibility of step i (Zi) is defined as the rate of the reverse reaction divided by the rate of the forward reaction:

$$Z_1 = \frac{r_{-1}}{r_1} = \frac{k_{-1}[INT1]}{k_1[R]^2} = \frac{[INT1]}{K_{eq,1}[R]^2}$$

$$Z_2 = \frac{r_{-2}}{r_2} = \frac{k_{-2}[INT2][H_2O]}{k_2[INT1]} = \frac{[INT2][H_2O]}{K_{eq,2}[INT1]}$$

$$Z_3 = \frac{r_{-3}}{r_3} = \frac{k_{-3}[INT3]}{k_3[INT2]} = \frac{[INT3]}{K_{eq,3}[INT2]}$$

$$Z_4 = \frac{r_{-4}}{r_4} = \frac{k_{-4}[P][H_2O]'}{k_4[INT3]} = \frac{[P][H_2O]'}{K_{eq,4}[INT3]}$$

From these equations, concentrations of the intermediates can be obtained:

$$[INT1] = Z_1 K_{eq,1}[R]^2$$

$$[INT2] = Z_2 K_{eq,2}\frac{[INT1]}{[H_2O]} = Z_1 Z_2 K_{eq,1} K_{eq,2}\frac{[R]^2}{[H_2O]}$$

$$[INT3] = Z_3 K_{eq,3}[INT2] = Z_1 Z_2 Z_3 K_{eq,1} K_{eq,2} K_{eq,3}\frac{[R]^2}{[H_2O]}$$

The reversibility of the overall reaction (β) is also obtained:

$$\beta = Z_1 Z_2 Z_3 Z_4 = \frac{[INT1]}{K_{eq,1}[R]^2}\frac{[INT2][H_2O]}{K_{eq,2}[INT1]}\frac{[INT3]}{K_{eq,3}[INT2]}\frac{[P][H_2O]'}{K_{eq,4}[INT3]}$$

$$\beta = \frac{[P][H_2O][H_2O]'}{K_{eq,1}K_{eq,2}K_{eq,3}K_{eq,4}[R]^2}$$

After that, it is possible to write expressions for the net rate of each step, considering that the net rates of all elementary steps are equal to the net rate of the overall reaction:

$$r = r_1 - r_{-1} = r_1(1 - Z_1) = k_1[R]^2(1 - Z_1)$$

$$r = r_2 - r_{-2} = r_2(1 - Z_2) = k_2[INT1](1 - Z_2) = K_{eq,1}k_2[R]^2 Z_1(1 - Z_2)$$

$$r = r_3 - r_{-3} = r_3(1 - Z_3) = k_3[INT2](1 - Z_3) = K_{eq,1}K_{eq,2}k_3\frac{[R]^2}{[H_2O]}Z_1Z_2(1 - Z_3)$$

$$r = r_4 - r_{-4} = r_4(1 - Z_4) = k_4[INT3](1 - Z_4) = K_{eq,1}K_{eq,2}K_{eq,3}k_4\frac{[R]^2}{[H_2O]}Z_1Z_2Z_3\left(1 - \frac{\beta}{Z_1Z_2Z_3}\right)$$

Where the concentrations of the intermediates have been replaced by their corresponding expressions in terms of concentrations of reactive, product, and byproducts. Z_4 was also replaced by the reversibility of the overall reaction (β) and the reversibilities of steps 1, 2, and 3.

It can be noticed that the net rates are controlled by the four following lumped parameters, Ci:

$$C_1 = k_1 = \nu^\dagger k_{TS_1}^\dagger = \frac{k_B T}{h}K_{eqR\to TS_1}^\dagger$$

$$C_2 = K_{eq,1}k_2 = \nu^\dagger K_{eq,1}k_{TS_2}^\dagger = \frac{k_B T}{h}K_{eqR\to TS_2}^\dagger$$

$$C_3 = K_{eq,1}K_{eq,2}k_3 = \nu^\dagger K_{eq,1}K_{eq,2}k_{TS_3}^\dagger = \frac{k_B T}{h}K_{eqR\to TS_3}^\dagger$$

$$C_4 = K_{eq,1}K_{eq,2}K_{eq,3}k_4 = \nu^\dagger K_{eq,1}K_{eq,2}K_{eq,3}k_{TS_4}^\dagger = \frac{k_B T}{h}K_{eqR\to TS_4}^\dagger$$

Where the expression $k_i = \nu^\dagger k_{TS_i}^\dagger$ has been used according to transition state theory: the rate constant of step i is expressed in terms of a frequency factor ($\nu^\dagger = k_B T/h$) times the equilibrium constant for the formation of the transition state.

The condensation of all constants into $K_{eqR\to TS_i}^\dagger$ represents the equilibrium constant for the formation of the transition state for step i from the reactant R.

To assess if an elementary step may contribute significantly to a reaction scheme, the maximum rate of this step can be estimated. This maximum rate corresponds to the case where the reversibility of step i is equal to the overall reversibility (β), while the rest of reversibilities of the other steps are equal to zero. Thus, if $Z_i = \beta$ and $Z_{j\neq i} = 1$:

$$r_1 = \frac{k_B T}{h}K_{eqR\to TS_1}^\dagger[R]^2(1 - \beta) = r_{max,1}(1 - \beta)$$

$$r_2 = \frac{k_B T}{h}K_{eqR\to TS_2}^\dagger[R]^2(1 - \beta) = r_{max,2}(1 - \beta)$$

$$r_3 = \frac{k_B T}{h}K_{eqR\to TS_3}^\dagger\frac{[R]^2}{[H_2O]}(1 - \beta) = r_{max,3}(1 - \beta)$$

$$r_4 = \frac{k_B T}{h}K_{eqR\to TS_4}^\dagger\frac{[R]^2}{[H_2O]}(1 - \beta) = r_{max,4}(1 - \beta)$$

Here, it can be generalized an expression for $r_{max,i}$, as follows:

$$r_{max,i} = \frac{k_B T}{h}K_{eq,A\to TS_i}^\dagger[CF] \quad (1)$$

Where [CF] represents the concentration factor which is different for each step, as can be seen above in each specific expression of $r_{max,i}$.

Now, in order to estimate the degrees of rate control for each step, it is necessary to solve the expressions of reversibilities (Z_i) in terms of the maximum rates ($r_{max,i}$).

Noticing that the net rates of all steps are equal to the net rate of the overall reaction, we have:

$$r = r_{max,1}(1 - Z_1)$$
$$r = r_{max,2}Z_1(1 - Z_2)$$
$$r = r_{max,3}Z_1Z_2(1 - Z_3)$$
$$r = r_{max,4}Z_1Z_2Z_3\left(1 - \frac{\beta}{Z_1Z_2Z_3}\right)$$

The following expressions for reversibilities can be obtained:

$$Z_1 = \frac{r_{max,1}r_{max,2}r_{max,3} + \beta r_{max,2}r_{max,3}r_{max,4} + r_{max,3}r_{max,4}r_{max,1} + r_{max,4}r_{max,1}r_{max,2}}{r_{max,1}r_{max,2}r_{max,3} + r_{max,2}r_{max,3}r_{max,4} + r_{max,3}r_{max,4}r_{max,1} + r_{max,4}r_{max,1}r_{max,2}}$$

$$Z_2 = \frac{r_{max,1}r_{max,2}r_{max,3} + \beta r_{max,2}r_{max,3}r_{max,4} + \beta r_{max,3}r_{max,4}r_{max,1} + r_{max,4}r_{max,1}r_{max,2}}{r_{max,1}r_{max,2}r_{max,3} + \beta r_{max,2}r_{max,3}r_{max,4} + r_{max,3}r_{max,4}r_{max,1} + r_{max,4}r_{max,1}r_{max,2}}$$

$$Z_3 = \frac{r_{max,1}r_{max,2}r_{max,3} + \beta r_{max,2}r_{max,3}r_{max,4} + \beta r_{max,3}r_{max,4}r_{max,1} + \beta r_{max,4}r_{max,1}r_{max,2}}{r_{max,1}r_{max,2}r_{max,3} + \beta r_{max,2}r_{max,3}r_{max,4} + \beta r_{max,3}r_{max,4}r_{max,1} + r_{max,4}r_{max,1}r_{max,2}}$$

The next phase is to express the degree of rate control in terms of $r_{max,i}$. Considering the definition of the degree of rate control for step i ($X_{RC,i}$):

$$X_{RC,i} = \left(\frac{\partial r}{\partial k_i}\right)\frac{k_i}{r}\Big|_{K_{eq,i}k_{j\neq i}} \tag{2}$$

While the sensitivity, s_i, for each step is defined as:

$$s_i = \left(\frac{\partial r}{\partial k_i}\right)\frac{k_i}{r}\Big|_{k_{j\neq i}} \tag{3}$$

Thus, the degree of rate control can be expressed as follows:

$$X_{RC,i} = s_i(1 - Z_i) \tag{4}$$

And, for each step of the reaction scheme, degrees of rate control in terms of the sensitivity can be written as:

$$X_{RC,1} = s_1(1 - Z_1)$$
$$X_{RC,2} = s_1Z_1(1 - Z_2)$$
$$X_{RC,3} = s_1Z_1Z_2(1 - Z_3)$$
$$X_{RC,4} = s_1Z_1Z_2Z_3\left(1 - \frac{\beta}{Z_1Z_2Z_3}\right)$$

Finally, the values of Z_i can then be expressed in terms of $r_{max,i}$, and the value of s_1 is obtained by requiring that the sum of $X_{RC,i}$ be equal to unity, leading to the following result:

$$X_{RC,1} = \frac{r_{max,2}r_{max,3}r_{max,4}}{r_{max,2}r_{max,3}r_{max,4} + r_{max,1}r_{max,3}r_{max,4} + r_{max,1}r_{max,2}r_{max,4} + r_{max,1}r_{max,2}r_{max,3}}$$

$$X_{RC,2} = \frac{r_{max,1}r_{max,3}r_{max,4}}{r_{max,2}r_{max,3}r_{max,4} + r_{max,1}r_{max,3}r_{max,4} + r_{max,1}r_{max,2}r_{max,4} + r_{max,1}r_{max,2}r_{max,3}}$$

$$X_{RC,3} = \frac{r_{max,1}r_{max,2}r_{max,4}}{r_{max,2}r_{max,3}r_{max,4} + r_{max,1}r_{max,3}r_{max,4} + r_{max,1}r_{max,2}r_{max,4} + r_{max,1}r_{max,2}r_{max,3}}$$

$$X_{RC,1} = \frac{r_{max,1}r_{max,2}r_{max,3}}{r_{max,2}r_{max,3}r_{max,4} + r_{max,1}r_{max,3}r_{max,4} + r_{max,1}r_{max,2}r_{max,4} + r_{max,1}r_{max,2}r_{max,3}}$$

Which can be generalized as follows:

$$X_{RC,i} = \frac{\Pi_{j=1,j\neq i}^{n} r_{max,j}}{\Sigma_{j=k}^{n}\left(\Pi_{j=1,j\neq k}^{n} r_{max,j}\right)} \quad (5)$$

Therefore, by determining the rate constants from values of enthalpy and entropy from DFT calculations, and using the presented equations, results for degrees of rate control for the present reaction scheme are shown in Table 1. Due to the fact that the process is carried oud in gas-phase, concentrations [R] and [H_2O] are replaced by the partial pressures P_R and P_{H2O}, and both are considered as 1 atm.

Table 1. Rate constants, equilibrium constants, maximum rates, and degrees of rate-control for elementary steps on the mechanism of formation of 2,5-diketopiperazine from pyrolysis of proline

i	$\boldsymbol{k_i}$ $\frac{k_B T}{h} e^{-\frac{\Delta G_i^{qh}}{RT}}$ (s^{-1})	$\boldsymbol{K_{eq,i}}$ k_i/k_{-1} (dimensionless)	**Expression for $r_{max,i}$**	$\boldsymbol{r_{max,i}}$ eq.(2) (s^{-1})	$\boldsymbol{X_{RC,i}}$ eq.(1) (dimensionless)
1	1.10×10^{-10}	4.59×10^{-10}	$k_1[R]^2$	1.10×10^{-10}	4.14×10^{-3}
-1	2.39×10^{-1}	---	---	---	---
2	9.94×10^{-4}	9.81×10^{6}	$k_{eq,1}k_2[R]^2$	4.56×10^{-13}	9.96×10^{-1}
-2	1.01×10^{-10}	---	---	---	---
3	1.82×10^{1}	5.03×10^{0}	$k_{eq,1}k_{eq,2}k_3\,[R]^2[H_2O]^{-1}$	8.22×10^{-2}	5.53×10^{-12}
-3	3.63×10^{0}	---	---	---	---
4	1.83×10^{3}	5.19×10^{11}	$k_{eq,1}k_{eq,2}k_{eq,3}k_4[R]^2[H_2O]^{-1}$	4.14×10^{1}	1.10×10^{-14}
-4	3.53×10^{-9}	---	---	---	---

Note: For the determination of rate constants (k_i), quasi-harmonic corrected Gibbs free energies (ΔG_i^{qh}) were obtained by using the Goodvibes v 2.0.3 program. The temperature (T) used in calculations was 573.15 K. k_B and h are the Boltzman's and Plank's constants, respectively.

B. Cartesian coordinates for each of the optimized transition states

Geometry of transition states were optimized by Gaussian calculations[2] at DFT wb97xd/6-311g(d,p) level of theory. The corresponding Cartesian coordinates of each structure, denoted as TS_i (see Scheme 1 in the main document), are presented as follows:

TS1

Atom symbol	Coordinates (Angstroms) X	Y	Z
N	1.758733	0.386769	1.036967

TS2

Atom symbol	Coordinates (Angstroms) X	Y	Z
N	-1.889674	0.483554	-0.897440

C	3.153479	0.865096	1.091220
C	1.425397	-0.015268	-0.330899
H	3.739095	0.221833	1.756431
H	3.210116	1.883068	1.486321
C	3.671015	0.769676	-0.350511
C	2.787437	-0.318044	-0.959824
H	0.945063	0.787049	-0.908766
C	0.529263	-1.261359	-0.334767
H	4.736461	0.538731	-0.400850
H	3.507498	1.717449	-0.873715
H	3.115960	-1.311942	-0.643905
H	2.742700	-0.310009	-2.047456
O	0.834429	-2.058828	0.738900
O	0.367439	-1.877355	-1.492152
N	-1.092977	-0.922774	-0.181628
C	-1.850407	-1.273930	1.034510
C	-1.682102	0.275007	-0.766830
H	-1.313809	-0.910370	1.911128
H	-1.920455	-2.358422	1.100443
C	-3.219383	-0.580028	0.870998
C	-3.187276	0.032684	-0.540340
H	-1.410222	0.315185	-1.826335
C	-1.280979	1.574111	-0.074236
H	-3.332443	0.204462	1.620685
H	-4.051327	-1.275058	0.986994
H	-3.789474	0.939309	-0.630061
H	-3.535395	-0.683769	-1.287527
O	-0.919819	1.655936	1.065342
O	-1.427054	2.684871	-0.818521
H	1.091682	1.051422	1.405095
H	-0.872333	-1.715263	-1.081538
H	-1.690469	2.458567	-1.714334
H	1.248446	-1.444869	1.375540

C	-3.083261	1.245428	-0.541401
C	-1.332926	0.022578	0.374498
H	-3.712579	1.411415	-1.417799
H	-2.824195	2.227179	-0.116499
C	-3.747109	0.359825	0.521058
C	-2.573550	-0.406790	1.175056
H	-0.837959	0.839953	0.917158
C	-0.300442	-1.100586	0.132322
H	-4.440102	-0.338504	0.046768
H	-4.318041	0.948972	1.240189
H	-2.710191	-1.486352	1.116959
H	-2.449481	-0.169376	2.231552
O	-0.948983	-1.935691	-1.093834
O	-0.318532	-2.134760	0.951327
N	0.946163	-0.604386	-0.357622
C	1.922029	-1.637556	-0.736376
C	1.602140	0.440576	0.409350
H	2.188151	-1.517139	-1.791510
H	1.491030	-2.626435	-0.594070
C	3.123218	-1.393506	0.169918
C	3.113058	0.124744	0.306513
H	1.312099	0.405054	1.471802
C	1.305366	1.851599	-0.098510
H	4.059480	-1.776832	-0.238990
H	2.945530	-1.860794	1.142619
H	3.530464	0.590384	-0.591710
H	3.675148	0.488605	1.169917
O	0.623311	2.132515	-1.039363
O	1.895227	2.830199	0.619769
H	-1.200038	1.035043	-1.400844
H	-0.983649	-2.561745	-0.134303
H	2.416549	2.453435	1.333603
H	-1.716966	-1.393023	-1.377162

TS3

Atom symbol	Coordinates (Angstroms) X	Y	Z
N	-1.211564	-0.482878	0.214628
C	-2.524416	-1.065533	-0.073965
C	-1.188364	0.804343	-0.496583
H	-2.753191	-1.840610	0.655608
H	-2.500658	-1.528764	-1.066354
C	-3.469411	0.153957	-0.030178
C	-2.551712	1.397573	-0.175686
H	-1.108748	0.592185	-1.574403
C	0.047490	1.587997	-0.072719
H	-4.014147	0.186574	0.914039
H	-4.208638	0.095967	-0.830170
H	-2.484038	1.961348	0.755719
H	-2.884524	2.086613	-0.951150
O	0.011998	2.739454	0.311583
N	1.169745	0.840337	-0.169955
C	2.471368	1.303258	0.300093
C	1.171469	-0.564396	-0.576190
H	2.482243	1.322274	1.394790
H	2.666411	2.312790	-0.063237
C	3.422128	0.244990	-0.255288

TS4

Atom symbol	Coordinates (Angstroms) X	Y	Z
N	-1.208425	-0.565393	-0.494953
C	-2.479649	-1.091495	0.023185
C	-1.230228	0.903461	-0.615990
H	-2.322166	-1.374415	1.067298
H	-2.785650	-1.969429	-0.544503
C	-3.427096	0.098568	-0.109056
C	-2.511815	1.304257	0.111365
H	-1.291093	1.169523	-1.679872
C	0.025725	1.569916	-0.052059
H	-4.243184	0.050049	0.612054
H	-3.863260	0.128389	-1.112295
H	-2.288206	1.434928	1.172406
H	-2.916559	2.242565	-0.264809
O	-0.014150	2.642371	0.515605
N	1.164789	0.881723	-0.284952
C	2.440090	1.262109	0.312435
C	1.164079	-0.491183	-0.778121
H	2.356436	1.245608	1.405142
H	2.715390	2.274162	0.013965
C	3.391485	0.183796	-0.205620

C	2.583120	-1.036351	-0.219878	C	2.503825	-1.061247	-0.314741
H	0.987851	-0.633074	-1.661273	H	1.111849	-0.500229	-1.877754
C	0.094447	-1.361528	0.202234	C	-0.072904	-1.217756	-0.301297
H	4.338276	0.163319	0.330579	H	4.246514	0.033846	0.454129
H	3.698133	0.495298	-1.284235	H	3.772393	0.466813	-1.191305
H	2.544543	-1.442490	0.793805	H	2.367402	-1.526292	0.661484
H	2.944072	-1.811140	-0.896605	H	2.888933	-1.811773	-1.003907
O	0.250854	-1.397798	1.513736	O	-0.084399	-2.526739	-0.178670
O	-0.131515	-2.606330	-0.383258	O	0.184555	-1.300202	1.693039
H	-0.806811	-0.588836	1.353706	H	0.165148	-2.448073	0.862448
H	0.004550	-2.542138	-1.331044	H	0.882370	-0.915975	2.224474

C. Electronic energy through the intrinsic reaction coordinate (IRC) for each step of the mechanism

Gaussian calculations[2] to determine the electronic energy from each transition state to both, forward and reverse directions over the corresponding reaction coordinate, were developed. The normalized data is presented, as follows:

Step 1: 2R → TS1 → INT1

Intrinsic Coordinate	Electronic Energy (kJ/mol)
0.000000	0.000000
0.000540	0.074619
0.001080	0.149499
0.001619	0.224635
0.002160	0.300032
0.002699	0.375688
0.003239	0.451602
0.003779	0.527773
0.004319	0.604201
0.004859	0.680889
0.005399	0.757832
0.005938	0.835032
0.006479	0.912490
0.007018	0.990202
0.007558	1.068172
0.008098	1.146396
0.008638	1.224877
0.009178	1.303611
0.009718	1.382599
0.010258	1.461839
0.010798	1.541334
0.011338	1.621083
0.011877	1.701085
0.012418	1.781336
0.012957	1.861842
0.013497	1.942597
0.014037	2.023604
0.014577	2.104863
0.015117	2.186372
0.015657	2.268130
0.016197	2.350140
0.016737	2.432400
0.017276	2.514909
0.017816	2.597667
0.018356	2.680675
0.018896	2.763935
0.019436	2.847441
0.019976	2.931200
0.020516	3.015211
0.021056	3.099471
0.021596	3.183981
0.022135	3.268745
0.022676	3.353759
0.023215	3.439027
0.023755	3.524547
0.024295	3.610322
0.024835	3.696352
0.025375	3.782637
0.025915	3.869181
0.026455	3.955980
0.026995	4.043039
0.027534	4.130358
0.028074	4.217939
0.028614	4.305783
0.029154	4.393890
0.029694	4.482261
0.030234	4.570901
0.030774	4.659808
0.031314	4.748983
0.031854	4.838432
0.032394	4.928153
0.032934	5.018147
0.033473	5.108417
0.034013	5.198965
0.034553	5.289794
0.035093	5.380902
0.035633	5.472290
0.036173	5.563965
0.036713	5.655923
0.037253	5.748170
0.037792	5.840703
0.038332	5.933528
0.038872	6.026644
0.039412	6.120048
0.039952	6.213750
0.040492	6.307745
0.041032	6.402038
0.041572	6.496626
0.042112	6.591512
0.042652	6.686697
0.043192	6.782184
0.043731	6.877970
0.044271	6.974055
0.044811	7.070445
0.045351	7.167135
0.045891	7.264128
0.046431	7.361424
0.046971	7.459024
0.047511	7.556924
0.048050	7.655131
0.048591	7.753640
0.049130	7.852450
0.049670	7.951563
0.050210	8.050980

0.050750	8.150697	0.083144	14.665111	0.115538	22.294727
0.051290	8.250715	0.083684	14.782660	0.116077	22.431805
0.051830	8.351035	0.084223	14.900521	0.116617	22.569202
0.052369	8.451655	0.084764	15.018700	0.117157	22.706920
0.052910	8.552574	0.085303	15.137197	0.117697	22.844956
0.053450	8.653790	0.085843	15.256014	0.118237	22.983315
0.053989	8.755305	0.086383	15.375149	0.118777	23.121991
0.054530	8.857116	0.086923	15.494604	0.119317	23.260990
0.055069	8.959225	0.087463	15.614381	0.119857	23.400310
0.055609	9.061627	0.088003	15.734480	0.120397	23.539949
0.056149	9.164324	0.088543	15.854904	0.120936	23.679915
0.056689	9.267314	0.089083	15.975653	0.121477	23.820201
0.057229	9.370596	0.089623	16.096725	0.122016	23.960812
0.057769	9.474167	0.090162	16.218126	0.122556	24.101746
0.058308	9.578029	0.090702	16.339852	0.123096	24.243008
0.058849	9.682182	0.091242	16.461909	0.123636	24.384596
0.059388	9.786622	0.091782	16.584291	0.124176	24.526513
0.059928	9.891348	0.092322	16.707002	0.124716	24.668757
0.060468	9.996363	0.092862	16.830040	0.125256	24.811332
0.061008	10.101661	0.093402	16.953413	0.125796	24.954238
0.061548	10.207246	0.093942	17.077111	0.126335	25.097477
0.062088	10.313114	0.094481	17.201142	0.126875	25.241050
0.062628	10.419265	0.095022	17.325504	0.127415	25.384957
0.063168	10.525698	0.095561	17.450197	0.127955	25.529204
0.063707	10.632414	0.096101	17.575218	0.128495	25.673788
0.064247	10.739413	0.096641	17.700572	0.129035	25.818710
0.064788	10.846694	0.097181	17.826260	0.129575	25.963976
0.065327	10.954256	0.097721	17.952276	0.130115	26.109584
0.065867	11.062101	0.098261	18.078626	0.130655	26.255538
0.066407	11.170224	0.098801	18.205304	0.131195	26.401836
0.066947	11.278631	0.099341	18.332315	0.131735	26.548484
0.067487	11.387319	0.099881	18.459657	0.132274	26.695480
0.068027	11.496287	0.100420	18.587327	0.132814	26.842826
0.068566	11.605540	0.100961	18.715331	0.133354	26.990523
0.069107	11.715073	0.101500	18.843662	0.133894	27.138575
0.069646	11.824890	0.102040	18.972325	0.134434	27.286984
0.070186	11.934990	0.102580	19.101319	0.134974	27.435748
0.070726	12.045374	0.103120	19.230638	0.135514	27.584868
0.071266	12.156041	0.103660	19.360287	0.136054	27.734348
0.071806	12.266998	0.104200	19.490265	0.136593	27.884188
0.072346	12.378240	0.104739	19.620572	0.137133	28.034391
0.072886	12.489769	0.105280	19.751203	0.137673	28.184955
0.073426	12.601586	0.105819	19.882163	0.138213	28.335879
0.073965	12.713695	0.106359	20.013449	0.138753	28.487171
0.074505	12.826095	0.106899	20.145060	0.139293	28.638825
0.075046	12.938784	0.107439	20.276996	0.139833	28.790847
0.075585	13.051770	0.107979	20.409256	0.140373	28.943234
0.076125	13.165050	0.108519	20.541841	0.140912	29.095985
0.076665	13.278624	0.109059	20.674749	0.141453	29.249104
0.077205	13.392497	0.109599	20.807980	0.141993	29.402591
0.077745	13.506667	0.110139	20.941537	0.142532	29.556445
0.078285	13.621139	0.110678	21.075411	0.143072	29.710665
0.078825	13.735912	0.111219	21.209608	0.143612	29.865252
0.079365	13.850985	0.111758	21.344128	0.144152	30.020206
0.079904	13.966366	0.112298	21.478966	0.144692	30.175525
0.080444	14.082053	0.112838	21.614127	0.145232	30.331212
0.080984	14.198045	0.113378	21.749608	0.145772	30.487264
0.081524	14.314344	0.113918	21.885407	0.146312	30.643678
0.082064	14.430956	0.114458	22.021528	0.146851	30.800460
0.082604	14.547877	0.114997	22.157968	0.147392	30.957601

0.147931	31.115108	0.180325	41.185428	0.212719	52.436961
0.148471	31.272974	0.180865	41.363245	0.213259	52.634822
0.149011	31.431200	0.181405	41.541388	0.213798	52.833036
0.149551	31.589785	0.181945	41.719859	0.214339	53.031613
0.150091	31.748727	0.182485	41.898656	0.214878	53.230547
0.150631	31.908027	0.183024	42.077781	0.215418	53.429841
0.151170	32.067681	0.183564	42.257236	0.215958	53.629497
0.151711	32.227690	0.184104	42.437015	0.216498	53.829513
0.152251	32.388050	0.184644	42.617124	0.217038	54.029889
0.152790	32.548759	0.185184	42.797559	0.217578	54.230629
0.153330	32.709821	0.185724	42.978322	0.218118	54.431729
0.153870	32.871226	0.186264	43.159410	0.218658	54.633189
0.154410	33.032980	0.186804	43.340830	0.219198	54.835014
0.154950	33.195079	0.187344	43.522572	0.219737	55.037199
0.155490	33.357518	0.187884	43.704645	0.220278	55.239743
0.156030	33.520302	0.188424	43.887041	0.220817	55.442649
0.156570	33.683424	0.188963	44.069768	0.221357	55.645916
0.157109	33.846888	0.189503	44.252818	0.221897	55.849539
0.157650	34.010685	0.190043	44.436196	0.222437	56.053522
0.158189	34.174821	0.190583	44.619903	0.222977	56.257859
0.158729	34.339290	0.191123	44.803934	0.223517	56.462554
0.159269	34.504093	0.191663	44.988292	0.224057	56.667605
0.159809	34.669229	0.192203	45.172975	0.224597	56.873006
0.160349	34.834696	0.192743	45.357986	0.225136	57.078761
0.160889	35.000491	0.193282	45.543320	0.225676	57.284866
0.161428	35.166617	0.193823	45.728985	0.226216	57.491317
0.161969	35.333071	0.194362	45.914972	0.226756	57.698117
0.162508	35.499850	0.194902	46.101288	0.227296	57.905258
0.163048	35.666958	0.195442	46.287933	0.227836	58.112743
0.163589	35.834391	0.195982	46.474902	0.228376	58.320568
0.164128	36.002150	0.196522	46.662200	0.228916	58.528730
0.164668	36.170232	0.197062	46.849824	0.229455	58.737229
0.165208	36.338640	0.197602	47.037778	0.229995	58.946061
0.165748	36.507370	0.198142	47.226060	0.230536	59.155222
0.166288	36.676426	0.198682	47.414671	0.231075	59.364713
0.166828	36.845802	0.199221	47.603610	0.231615	59.574527
0.167367	37.015504	0.199762	47.792882	0.232155	59.784665
0.167908	37.185526	0.200301	47.982483	0.232695	59.995122
0.168447	37.355874	0.200841	48.172417	0.233235	60.205894
0.168987	37.526542	0.201381	48.362684	0.233775	60.416982
0.169527	37.697533	0.201921	48.553282	0.234315	60.628382
0.170067	37.868849	0.202461	48.744216	0.234855	60.840089
0.170607	38.040486	0.203001	48.935484	0.235394	61.052101
0.171147	38.212446	0.203540	49.127091	0.235934	61.264417
0.171687	38.384731	0.204081	49.319033	0.236474	61.477033
0.172227	38.557337	0.204620	49.511314	0.237014	61.689943
0.172766	38.730268	0.205160	49.703936	0.237554	61.903146
0.173306	38.903522	0.205700	49.896898	0.238094	62.116641
0.173846	39.077102	0.206240	50.090200	0.238634	62.330425
0.174386	39.251004	0.206780	50.283846	0.239174	62.544490
0.174926	39.425233	0.207320	50.477839	0.239713	62.758841
0.175466	39.599786	0.207860	50.672176	0.240254	62.973468
0.176006	39.774663	0.208400	50.866860	0.240793	63.188371
0.176546	39.949868	0.208940	51.061892	0.241333	63.403549
0.177086	40.125396	0.209479	51.257272	0.241873	63.618995
0.177626	40.301252	0.210020	51.453005	0.242413	63.834711
0.178166	40.477433	0.210559	51.649088	0.242953	64.050690
0.178705	40.653943	0.211099	51.845525	0.243493	64.266931
0.179245	40.830778	0.211639	52.042314	0.244033	64.483435
0.179785	41.007939	0.212179	52.239461	0.244573	64.700194

0.245113	64.917207	0.277506	78.370826	0.309900	92.696578
0.245652	65.134473	0.278046	78.602668	0.310440	92.940723
0.246193	65.351990	0.278586	78.834783	0.310980	93.185007
0.246732	65.569754	0.279126	79.067174	0.311520	93.429434
0.247272	65.787763	0.279666	79.299841	0.312060	93.674007
0.247812	66.006018	0.280206	79.532780	0.312599	93.918727
0.248352	66.224512	0.280746	79.765996	0.313140	94.163597
0.248892	66.443248	0.281286	79.999484	0.313679	94.408616
0.249432	66.662220	0.281825	80.233245	0.314219	94.653791
0.249971	66.881428	0.282365	80.467280	0.314759	94.899123
0.250512	67.100870	0.282905	80.701582	0.315299	95.144615
0.251051	67.320545	0.283445	80.936155	0.315839	95.390267
0.251591	67.540455	0.283985	81.170995	0.316379	95.636088
0.252131	67.760592	0.284525	81.406101	0.316919	95.882079
0.252671	67.980961	0.285065	81.641472	0.317459	96.128240
0.253211	68.201555	0.285605	81.877102	0.317998	96.374578
0.253751	68.422378	0.286144	82.112993	0.318538	96.621096
0.254291	68.643427	0.286685	82.349141	0.319078	96.867801
0.254831	68.864702	0.287225	82.585541	0.319618	97.114690
0.255371	69.086202	0.287764	82.822193	0.320158	97.361776
0.255910	69.307928	0.288304	83.059095	0.320698	97.609054
0.256451	69.529877	0.288844	83.296238	0.321238	97.856533
0.256990	69.752052	0.289384	83.533625	0.321778	98.104218
0.257530	69.974451	0.289924	83.771248	0.322318	98.352112
0.258070	70.197075	0.290464	84.009105	0.322858	98.600217
0.258610	70.419922	0.291004	84.247194	0.323398	98.848542
0.259150	70.642997	0.291544	84.485508	0.323937	99.097085
0.259690	70.866296	0.292083	84.724045	0.324477	99.345856
0.260229	71.089823	0.292624	84.962803	0.325017	99.594856
0.260770	71.313576	0.293163	85.201773	0.325557	99.844089
0.261309	71.537558	0.293703	85.440953	0.326097	100.093562
0.261849	71.761770	0.294243	85.680341	0.326637	100.343276
0.262389	71.986211	0.294783	85.919931	0.327177	100.593239
0.262929	72.210886	0.295323	86.159721	0.327717	100.843449
0.263469	72.435791	0.295863	86.399702	0.328256	101.093917
0.264009	72.660933	0.296402	86.639875	0.328796	101.344641
0.264549	72.886311	0.296943	86.880234	0.329336	101.595631
0.265089	73.111926	0.297482	87.120775	0.329876	101.846884
0.265629	73.337779	0.298022	87.361493	0.330416	102.098409
0.266168	73.563874	0.298562	87.602388	0.330956	102.350210
0.266709	73.790213	0.299102	87.843451	0.331496	102.602287
0.267248	74.016796	0.299642	88.084685	0.332036	102.854648
0.267788	74.243626	0.300182	88.326079	0.332575	103.107292
0.268328	74.470706	0.300722	88.567638	0.333116	103.360227
0.268868	74.698035	0.301262	88.809352	0.333656	103.613454
0.269408	74.925618	0.301802	89.051221	0.334195	103.866980
0.269948	75.153454	0.302341	89.293242	0.334735	104.120806
0.270488	75.381547	0.302882	89.535413	0.335275	104.374936
0.271028	75.609897	0.303421	89.777733	0.335815	104.629373
0.271567	75.838507	0.303961	90.020198	0.336355	104.884125
0.272107	76.067380	0.304501	90.262805	0.336895	105.139190
0.272647	76.296515	0.305041	90.505556	0.337435	105.394575
0.273187	76.525916	0.305581	90.748446	0.337975	105.650283
0.273727	76.755584	0.306121	90.991478	0.338514	105.906322
0.274267	76.985520	0.306660	91.234649	0.339055	106.162688
0.274807	77.215724	0.307201	91.477957	0.339594	106.419391
0.275347	77.446198	0.307740	91.721404	0.340134	106.676436
0.275887	77.676946	0.308280	91.964990	0.340674	106.933827
0.276426	77.907966	0.308820	92.208715	0.341214	107.191564
0.276967	78.139259	0.309360	92.452577	0.341754	107.449656

0.342294	107.708108	0.374687	124.324727	0.407081	149.357246
0.342833	107.966924	0.375227	124.635510	0.407620	149.904335
0.343374	108.226108	0.375767	124.948341	0.408161	150.453679
0.343913	108.485671	0.376307	125.263309	0.408700	151.004819
0.344453	108.745611	0.376847	125.580498	0.409240	151.557421
0.344993	109.005940	0.377387	125.899998	0.409780	152.111252
0.345533	109.266662	0.377927	126.221905	0.410320	152.666159
0.346073	109.527784	0.378467	126.546314	0.410860	153.221982
0.346613	109.789315	0.379006	126.873328	0.411400	153.778499
0.347153	110.051259	0.379547	127.203052	0.411940	154.335360
0.347693	110.313628	0.380086	127.535590	0.412480	154.892060
0.348233	110.576424	0.380626	127.871045	0.413019	155.447965
0.348772	110.839660	0.381166	128.209524	0.413559	156.002332
0.349313	111.103344	0.381706	128.551120	0.414099	156.554388
0.349852	111.367488	0.382246	128.895924	0.414639	157.103375
0.350392	111.632096	0.382786	129.244018	0.415179	157.648594
0.350932	111.897180	0.383325	129.595473	0.415719	158.189389
0.351472	112.162754	0.383866	129.950349	0.416259	158.725125
0.352012	112.428828	0.384405	130.308695	0.416799	159.255116
0.352552	112.695413	0.384945	130.670568	0.417339	159.778612
0.353091	112.962521	0.385485	131.036024	0.417879	160.294770
0.353632	113.230167	0.386025	131.405136	0.418419	160.802675
0.354171	113.498362	0.386565	131.777993	0.418958	161.301397
0.354711	113.767124	0.387105	132.154711	0.419498	161.789995
0.355251	114.036466	0.387645	132.535432	0.420038	162.267565
0.355791	114.306404	0.388185	132.920309	0.420578	162.733221
0.356331	114.576954	0.388724	133.309518	0.421118	163.186096
0.356871	114.848137	0.389264	133.703228	0.421658	163.625319
0.357411	115.119968	0.389804	134.101595	0.422198	164.050001
0.357951	115.392466	0.390344	134.504748	0.422738	164.459251
0.358491	115.665654	0.390884	134.912775	0.423277	164.852157
0.359030	115.939552	0.391424	135.325719	0.423818	165.227801
0.359571	116.214179	0.391964	135.743572	0.424357	165.585244
0.360110	116.489562	0.392504	136.166283	0.424897	165.923532
0.360650	116.765726	0.393043	136.593762	0.425437	166.241685
0.361190	117.042692	0.393584	137.025903	0.425977	166.538731
0.361730	117.320486	0.394123	137.462610	0.426517	166.813718
0.362270	117.599141	0.394663	137.903807	0.427057	167.065727
0.362810	117.878678	0.395203	138.349481	0.427596	167.293909
0.363350	118.159128	0.395743	138.799699	0.428137	167.497485
0.363890	118.440524	0.396283	139.254606	0.428676	167.675751
0.364429	118.722897	0.396823	139.714415	0.429216	167.828075
0.364969	119.006275	0.397363	140.179367	0.429756	167.953891
0.365509	119.290695	0.397903	140.649694	0.430296	168.052681
0.366049	119.576192	0.398443	141.125548	0.430836	168.123948
0.366589	119.862800	0.398982	141.606954	0.431375	168.167197
0.367129	120.150554	0.399522	142.093798	0.431916	168.181911
0.367669	120.439496	0.400062	142.585827	0.432456	168.167513
0.368209	120.729661	0.400602	143.082682	0.432995	168.123441
0.368748	121.021097	0.401142	143.583969	0.433535	168.049118
0.369289	121.313842	0.401682	144.089330	0.434075	167.943996
0.369828	121.607943	0.402222	144.598512	0.434615	167.807601
0.370368	121.903448	0.402762	145.111393	0.435155	167.639572
0.370908	122.200411	0.403301	145.628005	0.435694	167.439653
0.371448	122.498878	0.403842	146.148492	0.436235	167.207698
0.371988	122.798909	0.404381	146.673043	0.436774	166.943649
0.372528	123.100566	0.404921	147.201816	0.437314	166.647500
0.373068	123.403906	0.405461	147.734842	0.437854	166.319302
0.373608	123.709002	0.406001	148.271996	0.438394	165.959134
0.374148	124.015918	0.406541	148.812951	0.438934	165.567118

0.439474	165.143399	0.471867	106.230516	0.504261	64.336940
0.440014	164.688124	0.472407	105.268979	0.504801	63.842774
0.440554	164.201432	0.472947	104.319769	0.505341	63.353853
0.441093	163.683411	0.473487	103.382691	0.505880	62.870139
0.441633	163.134111	0.474027	102.457462	0.506420	62.391607
0.442173	162.553579	0.474567	101.543751	0.506960	61.918232
0.442713	161.941911	0.475107	100.641223	0.507500	61.449993
0.443253	161.299323	0.475646	99.749579	0.508040	60.986873
0.443793	160.626197	0.476186	98.868580	0.508580	60.528852
0.444333	159.923101	0.476726	97.998042	0.509120	60.075919
0.444873	159.190744	0.477266	97.137816	0.509660	59.628051
0.445413	158.429922	0.477806	96.287768	0.510199	59.185237
0.445952	157.641437	0.478346	95.447758	0.510740	58.747453
0.446493	156.826054	0.478886	94.617635	0.511279	58.314684
0.447032	155.984471	0.479426	93.797235	0.511819	57.886906
0.447572	155.117339	0.479965	92.986391	0.512359	57.464090
0.448112	154.225309	0.480506	92.184954	0.512899	57.046210
0.448652	153.309070	0.481045	91.392778	0.513439	56.633232
0.449192	152.369375	0.481585	90.609746	0.513979	56.225119
0.449732	151.407037	0.482125	89.835741	0.514519	55.821829
0.450272	150.422926	0.482665	89.070649	0.515059	55.423323
0.450812	149.417948	0.483205	88.314332	0.515599	55.029551
0.451351	148.393037	0.483745	87.566634	0.516138	54.640472
0.451891	147.349180	0.484284	86.827364	0.516678	54.256039
0.452431	146.287425	0.484825	86.096310	0.517218	53.876208
0.452971	145.208928	0.485364	85.373239	0.517758	53.500940
0.453511	144.114937	0.485904	84.657922	0.518298	53.130190
0.454051	143.006797	0.486444	83.950152	0.518838	52.763923
0.454591	141.885914	0.486984	83.249766	0.519378	52.402100
0.455131	140.753703	0.487524	82.556642	0.519918	52.044685
0.455670	139.611551	0.488064	81.870725	0.520457	51.691642
0.456211	138.460791	0.488604	81.191999	0.520998	51.342942
0.456750	137.302691	0.489144	80.520480	0.521537	50.998544
0.457290	136.138468	0.489684	79.856189	0.522077	50.658419
0.457830	134.969302	0.490223	79.199134	0.522617	50.322533
0.458370	133.796362	0.490764	78.549286	0.523157	49.990851
0.458910	132.620826	0.491303	77.906577	0.523697	49.663336
0.459450	131.443870	0.491843	77.270886	0.524237	49.339950
0.459989	130.266690	0.492383	76.642073	0.524776	49.020658
0.460530	129.090476	0.492923	76.019964	0.525317	48.705419
0.461069	127.916432	0.493463	75.404381	0.525856	48.394193
0.461609	126.745732	0.494003	74.795157	0.526396	48.086933
0.462149	125.579534	0.494543	74.192138	0.526936	47.783596
0.462689	124.418950	0.495083	73.595191	0.527476	47.484131
0.463229	123.265006	0.495622	73.004212	0.528016	47.188495
0.463769	122.118642	0.496162	72.419122	0.528556	46.896631
0.464309	120.980698	0.496702	71.839874	0.529096	46.608488
0.464849	119.851930	0.497242	71.266443	0.529636	46.324015
0.465389	118.733044	0.497782	70.698823	0.530176	46.043155
0.465928	117.624710	0.498322	70.137019	0.530715	45.765852
0.466469	116.527556	0.498862	69.581048	0.531256	45.492052
0.467008	115.442138	0.499402	69.030917	0.531795	45.221696
0.467548	114.368883	0.499941	68.486624	0.532335	44.954733
0.468088	113.308060	0.500481	67.948150	0.532875	44.691103
0.468628	112.259761	0.501021	67.415457	0.533415	44.430756
0.469168	111.223965	0.501561	66.888490	0.533955	44.173631
0.469708	110.200579	0.502101	66.367182	0.534495	43.919679
0.470247	109.189536	0.502641	65.851449	0.535035	43.668844
0.470788	108.190819	0.503181	65.341215	0.535575	43.421078
0.471327	107.204463	0.503721	64.836402	0.536114	43.176324

0.536654	42.934534	0.561490	34.276139	0.779599	19.453705
0.537194	42.695658	0.562029	34.129016	0.784612	19.347055
0.537734	42.459646	0.562569	33.983277	0.789626	19.242749
0.538274	42.226449	0.563109	33.838904	0.794639	19.140790
0.538814	41.996020	0.563649	33.695882	0.799653	19.041158
0.539354	41.768310	0.564189	33.554200	0.804667	18.943841
0.539894	41.543273	0.564729	33.413843	0.809680	18.848814
0.540433	41.320862	0.565269	33.274799	0.814694	18.756055
0.540974	41.101029	0.565808	33.137100	0.819707	18.665530
0.541513	40.883732	0.574164	31.162902	0.824721	18.577214
0.542053	40.668924	0.582520	29.465950	0.829734	18.491068
0.542593	40.456563	0.590876	28.014568	0.834747	18.407065
0.543133	40.246599	0.599232	26.795590	0.839760	18.325173
0.543673	40.038993	0.607587	25.790273	0.844773	18.245369
0.544213	39.833703	0.615938	24.982746	0.849785	18.167654
0.544753	39.630686	0.624280	24.348118	0.854796	18.091982
0.545293	39.429898	0.629283	24.037303	0.859805	18.018541
0.545833	39.231300	0.634289	23.769494	0.864811	17.947031
0.546372	39.034852	0.639294	23.533619	0.869813	17.878292
0.546912	38.840518	0.644301	23.320707	0.874812	17.810465
0.547452	38.648258	0.649309	23.123346	0.879816	17.741572
0.547992	38.458033	0.654319	22.936557	0.884826	17.677444
0.548532	38.269808	0.659331	22.757291	0.889837	17.613201
0.549072	38.083550	0.664343	22.583805	0.894848	17.551657
0.549612	37.899224	0.669356	22.415093	0.899857	17.491614
0.550152	37.716796	0.674369	22.250543	0.904861	17.433346
0.550691	37.536233	0.679382	22.089757	0.909868	17.375034
0.551232	37.357507	0.684395	21.932461	0.914877	17.319082
0.551771	37.180585	0.689409	21.778454	0.919889	17.262886
0.552311	37.005441	0.694421	21.627614	0.924899	17.208937
0.552851	36.832047	0.699433	21.480014	0.929907	17.155792
0.553391	36.660371	0.704439	21.335889	0.934913	17.103709
0.553931	36.490394	0.709441	21.196693	0.939913	17.053119
0.554471	36.322086	0.714442	21.057432	0.944920	16.999926
0.555010	36.155424	0.719445	20.920501	0.949924	16.949346
0.555551	35.990386	0.724455	20.783067	0.954935	16.897589
0.556090	35.826948	0.729466	20.649773	0.959945	16.847923
0.556630	35.665089	0.734478	20.519280	0.964951	16.798519
0.557171	35.504786	0.739491	20.391400	0.969960	16.749406
0.557710	35.346022	0.744504	20.265969	0.974968	16.701882
0.558250	35.188776	0.749517	20.142904	0.979978	16.655056
0.558790	35.033026	0.754531	20.022189	0.984982	16.611192
0.559330	34.878759	0.759544	19.903808	0.989989	16.567929
0.559870	34.725953	0.764558	19.787766	0.994993	16.527578
0.560410	34.574593	0.769571	19.674063	1.000000	16.488471
0.560949	34.424661	0.774585	19.562711		

Step 2: INT1 → TS2 → INT2 + H_2O

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Intrinsic	Electronic	0.030017	0.358966	0.077179	1.393395
Coordinate	Energy	0.034305	0.425932	0.081465	1.527203
	(kJ/mol)	0.038594	0.499987	0.085747	1.662900
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0.000000	0.000000	0.047166	0.656527	0.094325	1.960364
0.004288	0.039490	0.051458	0.746669	0.098616	2.124988
0.008573	0.081666	0.055746	0.838522	0.102904	2.294556
0.012864	0.129461	0.060034	0.939929	0.107187	2.473021
0.017151	0.179734	0.064316	1.042208	0.111465	2.661173
0.021442	0.236032	0.068602	1.151001	0.115738	2.861813

0.120021	3.064494	0.238064	13.211120	0.263500	17.847298
0.124310	3.284858	0.238488	13.268067	0.263924	17.960565
0.128598	3.511913	0.238912	13.325442	0.264349	18.075796
0.132887	3.751955	0.239335	13.383245	0.264773	18.193043
0.137172	3.997770	0.239759	13.441486	0.265197	18.312358
0.141462	4.261150	0.240184	13.500171	0.265620	18.433796
0.145749	4.530878	0.240608	13.559305	0.266044	18.557412
0.150037	4.816614	0.241032	13.618896	0.266468	18.683260
0.154318	5.105377	0.241456	13.678952	0.266892	18.811398
0.158605	5.408992	0.241880	13.739483	0.267317	18.941877
0.162881	5.723359	0.242303	13.800494	0.267741	19.074762
0.167166	6.049924	0.242727	13.861994	0.268165	19.210109
0.171444	6.385912	0.243152	13.923998	0.268588	19.347974
0.175716	6.733116	0.243576	13.986511	0.269012	19.488420
0.180008	7.093127	0.244000	14.049547	0.269436	19.631507
0.184298	7.464247	0.244424	14.113115	0.269860	19.777301
0.188591	7.849111	0.244848	14.177230	0.270285	19.925862
0.192884	8.246076	0.245272	14.241901	0.270709	20.077259
0.197177	8.656087	0.245695	14.307145	0.271133	20.231552
0.201471	9.079475	0.246120	14.372972	0.271557	20.388811
0.205764	9.517338	0.246544	14.439399	0.271980	20.549106
0.210057	9.970494	0.246968	14.506441	0.272404	20.712504
0.214349	10.440865	0.247392	14.574111	0.272828	20.879073
0.218640	10.922868	0.247816	14.642432	0.273253	21.048888
0.222800	11.461707	0.248240	14.711414	0.273677	21.222019
0.223224	11.499658	0.248663	14.781087	0.274101	21.398539
0.223648	11.537941	0.249088	14.851458	0.274525	21.578522
0.224072	11.577350	0.249512	14.922594	0.274948	21.762050
0.224495	11.617767	0.249935	14.994425	0.275372	21.949193
0.224919	11.659100	0.250359	15.067193	0.275796	22.140033
0.225343	11.701271	0.250783	15.140434	0.276221	22.334645
0.225768	11.744213	0.251206	15.214788	0.276645	22.533112
0.226192	11.787873	0.251630	15.289350	0.277069	22.735515
0.226615	11.832202	0.252053	15.365088	0.277493	22.941931
0.227039	11.877161	0.252477	15.441505	0.277916	23.152447
0.227463	11.922713	0.252901	15.519015	0.278340	23.367139
0.227887	11.968833	0.253325	15.597463	0.278765	23.586095
0.228311	12.015493	0.253749	15.676921	0.279189	23.809391
0.228736	12.062671	0.254172	15.757377	0.279613	24.037112
0.229160	12.110347	0.254596	15.838862	0.280037	24.269340
0.229583	12.158507	0.255020	15.921397	0.280461	24.506154
0.230007	12.207136	0.255444	16.005011	0.280884	24.747637
0.230431	12.256220	0.255869	16.089736	0.281308	24.993870
0.230855	12.305747	0.256292	16.175606	0.281733	25.244931
0.231279	12.355711	0.256716	16.262652	0.282157	25.500896
0.231704	12.406104	0.257140	16.350913	0.282581	25.761847
0.232128	12.456918	0.257564	16.440419	0.283005	26.027857
0.232552	12.508150	0.257988	16.531214	0.283429	26.299006
0.232975	12.559791	0.258412	16.623332	0.283853	26.575361
0.233399	12.611841	0.258837	16.716816	0.284276	26.856996
0.233823	12.664299	0.259261	16.811701	0.284701	27.143981
0.234247	12.717158	0.259684	16.908031	0.285125	27.436388
0.234672	12.770421	0.260108	17.005849	0.285549	27.734278
0.235096	12.824087	0.260532	17.105198	0.285973	28.037717
0.235520	12.878156	0.260956	17.206117	0.286397	28.346767
0.235943	12.932628	0.261380	17.308653	0.286821	28.661489
0.236367	12.987506	0.261805	17.412857	0.287244	28.981936
0.236791	13.042791	0.262229	17.518775	0.287669	29.308170
0.237215	13.098486	0.262652	17.626454	0.288093	29.640236
0.237640	13.154595	0.263076	17.735946	0.288517	29.978190

0.288941	30.322075	0.314381	62.654005	0.339821	123.418813
0.289365	30.671939	0.314805	63.396772	0.340245	124.802722
0.289789	31.027823	0.315229	64.146746	0.340669	126.199102
0.290213	31.389772	0.315653	64.903943	0.341094	127.607644
0.290637	31.757817	0.316077	65.668389	0.341518	129.027961
0.291061	32.132001	0.316501	66.440105	0.341942	130.459486
0.291485	32.512352	0.316925	67.219130	0.342366	131.901402
0.291909	32.898907	0.317349	68.005494	0.342789	133.352668
0.292333	33.291692	0.317773	68.799245	0.343213	134.812063
0.292757	33.690736	0.318197	69.600443	0.343637	136.278237
0.293181	34.096066	0.318621	70.409160	0.344062	137.749767
0.293605	34.507705	0.319045	71.225499	0.344486	139.225219
0.294029	34.925677	0.319469	72.049591	0.344910	140.703189
0.294453	35.350000	0.319893	72.881591	0.345334	142.182330
0.294877	35.780695	0.320317	73.721664	0.345757	143.661371
0.295301	36.217780	0.320741	74.569981	0.346181	145.139087
0.295725	36.661272	0.321165	75.426693	0.346606	146.614261
0.296149	37.111185	0.321589	76.291913	0.347030	148.085649
0.296573	37.567531	0.322013	77.165721	0.347454	149.551977
0.296997	38.030320	0.322437	78.048162	0.347878	151.011928
0.297421	38.499565	0.322861	78.939257	0.348302	152.464169
0.297845	38.975274	0.323285	79.839016	0.348726	153.907338
0.298269	39.457453	0.323710	80.747463	0.349149	155.340068
0.298693	39.946106	0.324133	81.664636	0.349574	156.760954
0.299117	40.441241	0.324557	82.590603	0.349998	158.168564
0.299541	40.942858	0.324981	83.525454	0.350422	159.561410
0.299965	41.450969	0.325405	84.469319	0.350846	160.937959
0.300389	41.965572	0.325829	85.422367	0.351270	162.296648
0.300813	42.486679	0.326253	86.384810	0.351694	163.635907
0.301237	43.014291	0.326678	87.356904	0.352118	164.954210
0.301661	43.548423	0.327102	88.338933	0.352542	166.250128
0.302085	44.089082	0.327525	89.331183	0.352966	167.522385
0.302509	44.636278	0.327949	90.333919	0.353390	168.769886
0.302933	45.190019	0.328373	91.347357	0.353814	169.991741
0.303357	45.750322	0.328797	92.371641	0.354238	171.187252
0.303781	46.317196	0.329221	93.406852	0.354662	172.355862
0.304205	46.890648	0.329646	94.453024	0.355086	173.497065
0.304629	47.470689	0.330070	95.510171	0.355510	174.610324
0.305053	48.057328	0.330493	96.578327	0.355934	175.694976
0.305477	48.650578	0.330917	97.657597	0.356358	176.750204
0.305901	49.250442	0.331341	98.748177	0.356782	177.775026
0.306325	49.856932	0.331765	99.850409	0.357206	178.768347
0.306749	50.470055	0.332190	100.964739	0.357630	179.729023
0.307173	51.089820	0.332614	102.091719	0.358054	180.655940
0.307597	51.716230	0.333038	103.231903	0.358478	181.548066
0.308021	52.349288	0.333462	104.385784	0.358902	182.404520
0.308445	52.988994	0.333885	105.553696	0.359326	183.224613
0.308869	53.635352	0.334309	106.735783	0.359750	184.007871
0.309293	54.288364	0.334733	107.932010	0.360174	184.754043
0.309717	54.948031	0.335158	109.142253	0.360598	185.463080
0.310141	55.614368	0.335582	110.366416	0.361022	186.135093
0.310565	56.287396	0.336006	111.604560	0.361446	186.770291
0.310989	56.967149	0.336429	112.856955	0.361870	187.368905
0.311413	57.653672	0.336853	114.124050	0.362294	187.931119
0.311837	58.347022	0.337277	115.406336	0.362718	188.457017
0.312261	59.047267	0.337701	116.704179	0.363142	188.946531
0.312685	59.754469	0.338126	118.017648	0.363566	189.399440
0.313109	60.468691	0.338550	119.346471	0.363990	189.815403
0.313533	61.189995	0.338974	120.690079	0.364414	190.194037
0.313957	61.918421	0.339397	122.047754	0.364838	190.534990

0.365262	190.838059	0.390702	167.880217	0.416142	135.075968
0.365686	191.103235	0.391126	167.274764	0.416566	134.591967
0.366110	191.330763	0.391550	166.670978	0.416990	134.109863
0.366534	191.521117	0.391974	166.069197	0.417415	133.629651
0.366958	191.674977	0.392398	165.469583	0.417838	133.151327
0.367382	191.793158	0.392822	164.872132	0.418262	132.674888
0.367806	191.876536	0.393246	164.276700	0.418686	132.200329
0.368230	191.925988	0.393670	163.683067	0.419110	131.727644
0.368654	191.942331	0.394094	163.090985	0.419534	131.256821
0.369078	191.926282	0.394518	162.500250	0.419958	130.787854
0.369502	191.878500	0.394942	161.910739	0.420383	130.320723
0.369926	191.799565	0.395366	161.322435	0.420806	129.855416
0.370350	191.690021	0.395790	160.735420	0.421230	129.391907
0.370774	191.550431	0.396214	160.149876	0.421654	128.930176
0.371198	191.381412	0.396638	159.566031	0.422078	128.470199
0.371622	191.183688	0.397062	158.984131	0.422502	128.011952
0.372046	190.958097	0.397486	158.404404	0.422926	127.555410
0.372470	190.705616	0.397910	157.827028	0.423351	127.100544
0.372894	190.427336	0.398334	157.252109	0.423775	126.647333
0.373318	190.124438	0.398758	156.679685	0.424198	126.195752
0.373742	189.798143	0.399182	156.109731	0.424622	125.745784
0.374166	189.449663	0.399606	155.542181	0.425046	125.297403
0.374590	189.080161	0.400030	154.976948	0.425470	124.850593
0.375014	188.690718	0.400454	154.413933	0.425894	124.405342
0.375438	188.282334	0.400878	153.853061	0.426319	123.961630
0.375862	187.855951	0.401302	153.294270	0.426743	123.519446
0.376286	187.412496	0.401726	152.737533	0.427167	123.078780
0.376710	186.952955	0.402150	152.182833	0.427590	122.639615
0.377134	186.478382	0.402574	151.630186	0.428014	122.201942
0.377558	185.989890	0.402998	151.079616	0.428438	121.765751
0.377982	185.488579	0.403422	150.531157	0.428863	121.331032
0.378406	184.975470	0.403846	149.984851	0.429287	120.897774
0.378830	184.451441	0.404270	149.440735	0.429711	120.465966
0.379254	183.917241	0.404694	148.898845	0.430135	120.035597
0.379678	183.373545	0.405118	148.359202	0.430559	119.606658
0.380102	182.821045	0.405542	147.821820	0.430982	119.179138
0.380526	182.260527	0.405966	147.286696	0.431406	118.753027
0.380950	181.692883	0.406390	146.753816	0.431831	118.328313
0.381374	181.119065	0.406814	146.223153	0.432255	117.904988
0.381798	180.539998	0.407238	145.694684	0.432679	117.483041
0.382222	179.956470	0.407662	145.168382	0.433103	117.062465
0.382646	179.369059	0.408086	144.644222	0.433527	116.643249
0.383070	178.778124	0.408510	144.122191	0.433951	116.225385
0.383494	178.183845	0.408934	143.602274	0.434374	115.808865
0.383918	177.586339	0.409358	143.084467	0.434799	115.393687
0.384342	176.985774	0.409782	142.568767	0.435223	114.979845
0.384766	176.382461	0.410206	142.055164	0.435647	114.567331
0.385190	175.776899	0.410630	141.543648	0.436071	114.156149
0.385614	175.169747	0.411054	141.034209	0.436495	113.746293
0.386038	174.561705	0.411478	140.526826	0.436919	113.337765
0.386462	173.953411	0.411902	140.021478	0.437343	112.930563
0.386886	173.345327	0.412326	139.518146	0.437767	112.524690
0.387310	172.737678	0.412750	139.016804	0.438191	112.120150
0.387734	172.130453	0.413174	138.517434	0.438615	111.716947
0.388158	171.523466	0.413598	138.020020	0.439039	111.315083
0.388582	170.916471	0.414022	137.524546	0.439463	110.914563
0.389006	170.309269	0.414446	137.031002	0.439887	110.515392
0.389430	169.701807	0.414870	136.539377	0.440311	110.117576
0.389854	169.094230	0.415294	136.049669	0.440735	109.721121
0.390278	168.486876	0.415718	135.561867	0.441159	109.326030

0.441583	108.932310	0.467021	87.574716	0.492462	70.136449
0.442007	108.539966	0.467445	87.252312	0.492886	69.874595
0.442431	108.149000	0.467870	86.931069	0.493310	69.613652
0.442855	107.759413	0.468294	86.610994	0.493734	69.353620
0.443279	107.371211	0.468718	86.292091	0.494158	69.094509
0.443703	106.984394	0.469142	85.974368	0.494582	68.836323
0.444127	106.598960	0.469565	85.657828	0.495006	68.579066
0.444551	106.214910	0.469989	85.342473	0.495430	68.322743
0.444975	105.832238	0.470413	85.028304	0.495854	68.067363
0.445399	105.450944	0.470838	84.715323	0.496278	67.812929
0.445823	105.071021	0.471262	84.403529	0.496702	67.559442
0.446247	104.692464	0.471686	84.092919	0.497126	67.306914
0.446671	104.315263	0.472110	83.783488	0.497550	67.055344
0.447095	103.939410	0.472534	83.475234	0.497974	66.804734
0.447519	103.564895	0.472957	83.168150	0.498398	66.555091
0.447943	103.191707	0.473381	82.862229	0.498822	66.306417
0.448367	102.819834	0.473806	82.557461	0.499246	66.058712
0.448791	102.449260	0.474230	82.253841	0.499670	65.811975
0.449215	102.079970	0.474654	81.951354	0.500094	65.566210
0.449639	101.711954	0.475078	81.649991	0.500518	65.321413
0.450063	101.345193	0.475502	81.349742	0.500942	65.077583
0.450487	100.979673	0.475926	81.050595	0.501366	64.834719
0.450911	100.615377	0.476350	80.752535	0.501790	64.592816
0.451335	100.252292	0.476774	80.455552	0.502214	64.351869
0.451759	99.890406	0.477198	80.159634	0.502638	64.111872
0.452183	99.529715	0.477622	79.864764	0.503062	63.872823
0.452607	99.170257	0.478046	79.570931	0.503486	63.634713
0.453031	98.812021	0.478470	79.278125	0.503910	63.397534
0.453455	98.455405	0.478894	78.986330	0.504334	63.161278
0.453878	98.099644	0.479318	78.695532	0.504758	62.925939
0.454302	97.746289	0.479742	78.405724	0.505182	62.691505
0.454726	97.391513	0.480166	78.116893	0.505606	62.457970
0.455149	97.038837	0.480590	77.829028	0.506030	62.225321
0.455573	96.686469	0.481014	77.542118	0.506454	61.993553
0.455997	96.335571	0.481438	77.256157	0.506879	61.762653
0.456421	95.985702	0.481862	76.971130	0.507302	61.532612
0.456845	95.636915	0.482286	76.687032	0.507726	61.303424
0.457269	95.289157	0.482710	76.403856	0.508150	61.075079
0.457693	94.942423	0.483134	76.121594	0.508574	60.847567
0.458117	94.596699	0.483558	75.840240	0.508998	60.620878
0.458541	94.251987	0.483982	75.559790	0.509422	60.395012
0.458965	93.908283	0.484406	75.280234	0.509847	60.169954
0.459389	93.565581	0.484830	75.001574	0.510271	59.945705
0.459813	93.223886	0.485254	74.723802	0.510694	59.722254
0.460237	92.883201	0.485678	74.446914	0.511118	59.499598
0.460661	92.543527	0.486102	74.170911	0.511542	59.277733
0.461085	92.204866	0.486526	73.895787	0.511966	59.056653
0.461509	91.867230	0.486950	73.621543	0.512390	58.836358
0.461934	91.530619	0.487374	73.348176	0.512815	58.616845
0.462358	91.195044	0.487798	73.075689	0.513239	58.398109
0.462781	90.860510	0.488222	72.804075	0.513663	58.180153
0.463205	90.527030	0.488646	72.533339	0.514086	57.962969
0.463629	90.194613	0.489070	72.263482	0.514510	57.746562
0.464053	89.863264	0.489494	71.994502	0.514934	57.530927
0.464477	89.533000	0.489918	71.726402	0.515359	57.316064
0.464902	89.203828	0.490342	71.459187	0.515783	57.101971
0.465326	88.875758	0.490766	71.192856	0.516207	56.888649
0.465750	88.548802	0.491190	70.927413	0.516631	56.676094
0.466173	88.222970	0.491614	70.662862	0.517055	56.464305
0.466597	87.898272	0.492038	70.399204	0.517478	56.253280

0.517902	56.043015	0.543343	44.696591	0.631818	19.300392
0.518327	55.833510	0.543767	44.528047	0.639246	17.775575
0.518751	55.624759	0.544191	44.360138	0.646674	16.306482
0.519175	55.416759	0.544615	44.192860	0.654102	14.899048
0.519599	55.209508	0.545039	44.026209	0.661452	13.564858
0.520023	55.002999	0.545463	43.860180	0.668802	12.277198
0.520447	54.797225	0.545887	43.694773	0.676154	11.031768
0.520870	54.592182	0.546311	43.529984	0.683505	9.830132
0.521295	54.387868	0.546735	43.365811	0.690856	8.664218
0.521719	54.184271	0.547159	43.202256	0.698207	7.533720
0.522143	53.981388	0.547583	43.039317	0.705558	6.441677
0.522567	53.779214	0.548007	42.876993	0.712909	5.388277
0.522991	53.577738	0.548431	42.715283	0.717262	4.781036
0.523415	53.376961	0.548855	42.554193	0.721615	4.184519
0.523839	53.176869	0.549279	42.393728	0.725969	3.598145
0.524263	52.977462	0.549703	42.233885	0.730322	3.024421
0.524687	52.778733	0.550127	42.074711	0.734676	2.462974
0.525111	52.580673	0.550551	41.916139	0.739030	1.912251
0.525535	52.383283	0.550975	41.758352	0.743383	1.371131
0.525959	52.186557	0.551399	41.600956	0.747737	0.840937
0.526383	51.990490	0.551822	41.444384	0.752091	0.322327
0.526807	51.795079	0.552246	41.288077	0.756444	-0.183830
0.527231	51.600325	0.552670	41.132530	0.760795	-0.677825
0.527655	51.406221	0.553094	40.977504	0.765140	-1.156155
0.528079	51.212769	0.553518	40.823135	0.769488	-1.635868
0.528503	51.019968	0.553942	40.669363	0.773838	-2.097861
0.528927	50.827821	0.554366	40.516201	0.778191	-2.558240
0.529351	50.636325	0.554790	40.363639	0.782544	-3.004614
0.529775	50.445480	0.555214	40.211670	0.786897	-3.443010
0.530199	50.255294	0.555638	40.060291	0.791248	-3.870391
0.530623	50.065767	0.556062	39.909493	0.795599	-4.288528
0.531047	49.876899	0.556486	39.759275	0.799946	-4.694953
0.531471	49.688695	0.556910	39.609624	0.804293	-5.091884
0.531895	49.501159	0.557334	39.460538	0.808636	-5.480440
0.532319	49.314294	0.557758	39.312008	0.812982	-5.863327
0.532743	49.128104	0.558182	39.164024	0.817329	-6.240617
0.533167	48.942591	0.558607	39.016581	0.821679	-6.609040
0.533591	48.757759	0.559030	38.869669	0.826029	-6.968298
0.534015	48.573614	0.559454	38.723282	0.830381	-7.318589
0.534439	48.390155	0.559878	38.577404	0.834733	-7.660385
0.534863	48.207388	0.560302	38.432032	0.839085	-7.994267
0.535287	48.025313	0.560726	38.287157	0.843436	-8.320590
0.535711	47.843933	0.561150	38.142768	0.847784	-8.639129
0.536135	47.663246	0.561575	37.998856	0.852130	-8.950135
0.536559	47.483260	0.561999	37.855415	0.856478	-9.260973
0.536983	47.303967	0.562422	37.712430	0.860829	-9.559858
0.537407	47.125370	0.562846	37.569899	0.865181	-9.856747
0.537831	46.947471	0.563270	37.427813	0.869532	-10.144184
0.538255	46.770263	0.563694	37.286162	0.873881	-10.424844
0.538679	46.593748	0.564118	37.144941	0.878232	-10.703058
0.539103	46.417918	0.564543	37.004144	0.882579	-10.972303
0.539527	46.242777	0.564967	36.863779	0.886929	-11.238986
0.539951	46.068315	0.572395	34.469163	0.891278	-11.499511
0.540375	45.894530	0.579823	32.200655	0.895627	-11.754316
0.540799	45.721418	0.587251	30.053747	0.899977	-12.005823
0.541223	45.548972	0.594679	28.013859	0.904328	-12.252308
0.541647	45.377191	0.602107	26.086193	0.908675	-12.492646
0.542071	45.206066	0.609534	24.266436	0.913024	-12.729737
0.542495	45.035595	0.616962	22.534554	0.917373	-12.961083
0.542919	44.865770	0.624390	20.882529	0.921722	-13.186863

0.926071	-13.409557	0.952165	-14.655924	0.978258	-15.779654
0.930422	-13.627364	0.956515	-14.850881	0.982609	-15.956434
0.934769	-13.840011	0.960862	-15.042041	0.986956	-16.130085
0.939118	-14.050266	0.965211	-15.231573	0.991304	-16.302289
0.943467	-14.255690	0.969560	-15.416999	0.995654	-16.470200
0.947816	-14.456843	0.973909	-15.599085	1.000000	-16.636229

Step 3: INT2 → TS3 → INT3

Intrinsic Coordinate	Electronic Energy (kJ/mol)
0.000000	0.000000
0.001322	0.012164
0.002643	0.025013
0.003961	0.037847
0.005278	0.051347
0.006595	0.064810
0.007913	0.078852
0.009232	0.093334
0.010554	0.108252
0.011877	0.123766
0.013200	0.139619
0.014524	0.156096
0.015848	0.172855
0.017172	0.190262
0.018496	0.207884
0.019820	0.226145
0.021144	0.244631
0.022468	0.263695
0.023793	0.283126
0.025118	0.303067
0.026443	0.323480
0.027767	0.344324
0.029092	0.365695
0.030416	0.387432
0.031741	0.409736
0.033065	0.432354
0.034389	0.455566
0.035713	0.479064
0.037037	0.503135
0.038362	0.527515
0.039686	0.552442
0.041011	0.577747
0.042336	0.603581
0.043661	0.629831
0.044985	0.656601
0.046311	0.683783
0.047636	0.711474
0.048960	0.739538
0.050285	0.768101
0.051610	0.796994
0.052935	0.826387
0.054260	0.856120
0.055585	0.886343
0.056910	0.916935
0.058236	0.947997
0.059561	0.979430
0.060887	1.011319
0.062212	1.043571
0.063538	1.076279
0.064863	1.109313
0.066188	1.142801
0.067513	1.176542
0.068838	1.210710
0.070162	1.245141
0.071487	1.280007
0.072813	1.315228
0.074138	1.350880
0.075464	1.386926
0.076790	1.423381
0.078116	1.460253
0.079441	1.497535
0.080767	1.535303
0.082092	1.573386
0.083416	1.612060
0.084740	1.650570
0.086064	1.689669
0.087387	1.728629
0.088711	1.768303
0.090036	1.808305
0.091362	1.848885
0.092687	1.889869
0.094013	1.931323
0.095339	1.973181
0.096665	2.015483
0.097990	2.058187
0.099316	2.101343
0.100642	2.144907
0.101968	2.188945
0.103293	2.233400
0.104619	2.278349
0.105945	2.323720
0.107270	2.369606
0.108595	2.415901
0.109921	2.462706
0.111246	2.509923
0.112571	2.557639
0.113896	2.605819
0.115221	2.654509
0.116547	2.703724
0.117872	2.753464
0.119198	2.803756
0.120524	2.854570
0.121850	2.905948
0.123176	2.957846
0.124501	3.010312
0.125827	3.063284
0.127153	3.116826
0.128479	3.170850
0.129804	3.225445
0.131130	3.280515
0.132455	3.336155
0.133781	3.392290
0.135107	3.448999
0.136433	3.506234
0.137759	3.564056
0.139084	3.622439
0.140410	3.681494
0.141736	3.741127
0.143060	3.801338
0.144384	3.861538
0.145708	3.922140
0.147033	3.983319
0.148358	4.045234
0.149684	4.107805
0.151010	4.170982
0.152336	4.234745
0.153662	4.299093
0.154989	4.364030
0.156315	4.429576
0.157641	4.495767
0.158967	4.562633
0.160292	4.630169
0.161617	4.698177
0.162941	4.766522
0.164266	4.835341
0.165591	4.904886
0.166916	4.975223
0.168242	5.046321
0.169569	5.118155
0.170895	5.190713
0.172221	5.264001
0.173547	5.338027
0.174873	5.412831
0.176200	5.488408
0.177526	5.564884
0.178851	5.641989
0.180176	5.720019
0.181501	5.798246
0.182827	5.877457
0.184152	5.957396
0.185478	6.038351
0.186804	6.120198
0.188130	6.202951
0.189456	6.286589
0.190782	6.371112
0.192109	6.456530
0.193435	6.542846
0.194761	6.630068
0.196087	6.718206
0.197414	6.807268
0.198740	6.897257
0.200066	6.988186
0.201393	7.080057
0.202719	7.172877

0.204045	7.266651	0.283622	14.797250	0.363192	26.828498
0.205371	7.361380	0.284948	14.956851	0.364519	27.074048
0.206698	7.457071	0.286274	15.117682	0.365845	27.321108
0.208024	7.553729	0.287601	15.279748	0.367171	27.569669
0.209350	7.651350	0.288927	15.443075	0.368497	27.819719
0.210677	7.749940	0.290253	15.607676	0.369824	28.071253
0.212003	7.849502	0.291579	15.773563	0.371150	28.324256
0.213329	7.950035	0.292906	15.940757	0.372476	28.578720
0.214655	8.051539	0.294232	16.109272	0.373803	28.834635
0.215982	8.154021	0.295558	16.279124	0.375129	29.091995
0.217308	8.257476	0.296885	16.450325	0.376455	29.350787
0.218634	8.361908	0.298211	16.622889	0.377781	29.611009
0.219960	8.467319	0.299537	16.796828	0.379108	29.872650
0.221287	8.573715	0.300863	16.972154	0.380434	30.135707
0.222613	8.681098	0.302190	17.148876	0.381760	30.400171
0.223939	8.789470	0.303516	17.327003	0.383087	30.666040
0.225266	8.898838	0.304842	17.506550	0.384413	30.933308
0.226592	9.009212	0.306169	17.687513	0.385739	31.201972
0.227918	9.120596	0.307495	17.869914	0.387065	31.472031
0.229244	9.233001	0.308821	18.053747	0.388392	31.743476
0.230571	9.346433	0.310147	18.239049	0.389718	32.016311
0.231897	9.460908	0.311473	18.425775	0.391044	32.290531
0.233223	9.576432	0.312799	18.614013	0.392370	32.566132
0.234550	9.693018	0.314125	18.803534	0.393697	32.843115
0.235876	9.810680	0.315450	18.994526	0.395023	33.121481
0.237202	9.929423	0.316775	19.186595	0.396349	33.401228
0.238528	10.049264	0.318101	19.380147	0.397676	33.682358
0.239855	10.170210	0.319427	19.574974	0.399002	33.964878
0.241181	10.292272	0.320753	19.771359	0.400328	34.248786
0.242507	10.415458	0.322078	19.969183	0.401654	34.534094
0.243833	10.539776	0.323404	20.168500	0.402981	34.820809
0.245160	10.665235	0.324730	20.369251	0.404307	35.108937
0.246486	10.791837	0.326057	20.571441	0.405633	35.398498
0.247812	10.919586	0.327383	20.775049	0.406960	35.689501
0.249139	11.048485	0.328709	20.980076	0.408286	35.981966
0.250465	11.178536	0.330035	21.186517	0.409612	36.275909
0.251791	11.309738	0.331362	21.394378	0.410938	36.571354
0.253117	11.442089	0.332688	21.603659	0.412265	36.868324
0.254444	11.575588	0.334014	21.814366	0.413591	37.166841
0.255770	11.710231	0.335340	22.026509	0.414917	37.466927
0.257096	11.846014	0.336667	22.240099	0.416243	37.768610
0.258423	11.982932	0.337993	22.455137	0.417570	38.071916
0.259749	12.120980	0.339319	22.671641	0.418896	38.376863
0.261075	12.260153	0.340646	22.889618	0.420222	38.683474
0.262401	12.400447	0.341972	23.109079	0.421549	38.991770
0.263728	12.541859	0.343298	23.330035	0.422875	39.301769
0.265054	12.684381	0.344624	23.552499	0.424201	39.613478
0.266380	12.828012	0.345951	23.776475	0.425527	39.926911
0.267706	12.972753	0.347277	24.001980	0.426854	40.242068
0.269033	13.118600	0.348603	24.229015	0.428180	40.558950
0.270359	13.265557	0.349930	24.457588	0.429506	40.877549
0.271685	13.413622	0.351256	24.687708	0.430833	41.197857
0.273012	13.562800	0.352582	24.919377	0.432159	41.519851
0.274338	13.713097	0.353908	25.152597	0.433485	41.843512
0.275664	13.864520	0.355235	25.387372	0.434811	42.167531
0.276990	14.017077	0.356561	25.623699	0.436127	42.496674
0.278317	14.170779	0.357887	25.861577	0.443140	44.245703
0.279643	14.325631	0.359214	26.101001	0.450156	46.035370
0.280969	14.481654	0.360540	26.341967	0.457174	47.853592
0.282296	14.638853	0.361866	26.584469	0.464192	49.695249

0.471209	51.560126	0.634950	108.841255	0.660224	138.556830
0.478226	53.451426	0.635371	109.227537	0.660645	138.958783
0.485244	55.372115	0.635792	109.619590	0.661066	139.344550
0.492261	57.320840	0.636213	110.017403	0.661487	139.713325
0.499279	59.290285	0.636635	110.420995	0.661908	140.064289
0.506296	61.269616	0.637056	110.830413	0.662330	140.396586
0.513313	63.250151	0.637477	111.245730	0.662751	140.709314
0.520330	65.229626	0.637898	111.667065	0.663172	141.001545
0.527348	67.211338	0.638319	112.094541	0.663593	141.272321
0.534365	69.199970	0.638741	112.528279	0.664015	141.520691
0.541382	71.198535	0.639162	112.968339	0.664436	141.745715
0.548399	73.208652	0.639583	113.414682	0.664857	141.946510
0.555416	75.233296	0.640005	113.867160	0.665278	142.122272
0.562432	77.279447	0.640425	114.325518	0.665699	142.272287
0.569448	79.359243	0.640847	114.789438	0.666121	142.395972
0.576464	81.490550	0.641268	115.258626	0.666542	142.492848
0.583479	83.698194	0.641689	115.732857	0.666963	142.562531
0.590492	86.015940	0.642111	116.212021	0.667384	142.604686
0.597505	88.488831	0.642532	116.696139	0.667806	142.618977
0.604516	91.176429	0.642953	117.185320	0.668227	142.605007
0.611525	94.159396	0.643374	117.679725	0.668648	142.562324
0.618525	97.570031	0.643795	118.179507	0.669069	142.490369
0.618943	97.790008	0.644217	118.684743	0.669490	142.388513
0.619364	98.014470	0.644638	119.195376	0.669912	142.256078
0.619785	98.241374	0.645059	119.711190	0.670333	142.092393
0.620206	98.470748	0.645480	120.231819	0.670754	141.896851
0.620628	98.702666	0.645902	120.756795	0.671175	141.668940
0.621049	98.937210	0.646323	121.285639	0.671596	141.408291
0.621470	99.174469	0.646744	121.817936	0.672018	141.114718
0.621892	99.414534	0.647166	122.353383	0.672439	140.788213
0.622313	99.657503	0.647587	122.891805	0.672860	140.428961
0.622734	99.903486	0.648008	123.433099	0.673282	140.037283
0.623155	100.152588	0.648429	123.977189	0.673703	139.613596
0.623576	100.404925	0.648850	124.523970	0.674124	139.158316
0.623998	100.660615	0.649272	125.073270	0.674545	138.671771
0.624419	100.919775	0.649693	125.624824	0.674966	138.154138
0.624840	101.182525	0.650114	126.178285	0.675388	137.605417
0.625261	101.448984	0.650535	126.733221	0.675809	137.025436
0.625682	101.719263	0.650956	127.289123	0.676230	136.413938
0.626104	101.993479	0.651378	127.845414	0.676651	135.770667
0.626525	102.271737	0.651799	128.401472	0.677073	135.095475
0.626946	102.554138	0.652220	128.956676	0.677494	134.388391
0.627368	102.840785	0.652642	129.510451	0.677915	133.649675
0.627789	103.131767	0.653062	130.062326	0.678336	132.879818
0.628210	103.427180	0.653484	130.611917	0.678757	132.079524
0.628631	103.727107	0.653905	131.158885	0.679179	131.249667
0.629052	104.031641	0.654326	131.702857	0.679600	130.391207
0.629474	104.340867	0.654748	132.243300	0.680021	129.505140
0.629895	104.654880	0.655169	132.779480	0.680443	128.592414
0.630316	104.973786	0.655590	133.310474	0.680864	127.653874
0.630737	105.297707	0.656011	133.835251	0.681285	126.690231
0.631159	105.626774	0.656432	134.352800	0.681706	125.702064
0.631580	105.961139	0.656854	134.862226	0.682127	124.689852
0.632001	106.300955	0.657275	135.362762	0.682549	123.654056
0.632422	106.646376	0.657696	135.853738	0.682970	122.595184
0.632843	106.997529	0.658117	136.334493	0.683391	121.513869
0.633265	107.354511	0.658538	136.804300	0.683812	120.410925
0.633686	107.717373	0.658960	137.262340	0.684233	119.287361
0.634107	108.086135	0.659381	137.707722	0.684655	118.144360
0.634529	108.460776	0.659802	138.139522	0.685076	116.983243

0.685497	115.805410	0.710771	52.653008	0.736045	24.845395
0.685919	114.612283	0.711192	51.962767	0.736466	24.560539
0.686340	113.405267	0.711614	51.282889	0.736888	24.280044
0.686761	112.185696	0.712035	50.613192	0.737309	24.003854
0.687182	110.954838	0.712456	49.953451	0.737730	23.731905
0.687603	109.713895	0.712877	49.303416	0.738151	23.464143
0.688025	108.464021	0.713298	48.662842	0.738572	23.200506
0.688446	107.206367	0.713720	48.031488	0.738994	22.940944
0.688867	105.942104	0.714141	47.409137	0.739415	22.685394
0.689288	104.672465	0.714562	46.795607	0.739836	22.433805
0.689709	103.398743	0.714983	46.190744	0.740257	22.186123
0.690131	102.122299	0.715405	45.594420	0.740679	21.942293
0.690552	100.844549	0.715826	45.006536	0.741100	21.702260
0.690973	99.566934	0.716247	44.427007	0.741521	21.465970
0.691394	98.290893	0.716668	43.855753	0.741942	21.233369
0.691816	97.017851	0.717089	43.292702	0.742363	21.004402
0.692237	95.749173	0.717511	42.737760	0.742785	20.779021
0.692658	94.486158	0.717932	42.190832	0.743206	20.557169
0.693080	93.230014	0.718353	41.651796	0.743627	20.338793
0.693501	91.981851	0.718775	41.120521	0.744049	20.123846
0.693922	90.742683	0.719196	40.596870	0.744470	19.912270
0.694343	89.513445	0.719617	40.080697	0.744891	19.704020
0.694764	88.295035	0.720038	39.571869	0.745312	19.499048
0.695186	87.088336	0.720459	39.070260	0.745733	19.297302
0.695607	85.894230	0.720881	38.575755	0.746155	19.098735
0.696028	84.713590	0.721302	38.088260	0.746576	18.903303
0.696449	83.547204	0.721723	37.607680	0.746997	18.710962
0.696870	82.395715	0.722144	37.133940	0.747418	18.521669
0.697292	81.259566	0.722565	36.666956	0.747839	18.335379
0.697713	80.138982	0.722987	36.206653	0.748261	18.152053
0.698134	79.034032	0.723408	35.752956	0.748682	17.971653
0.698556	77.944720	0.723829	35.305784	0.749103	17.794140
0.698977	76.871080	0.724251	34.865059	0.749525	17.619478
0.699398	75.813242	0.724672	34.430702	0.749946	17.447629
0.699819	74.771404	0.725093	34.002638	0.750367	17.278563
0.700240	73.745790	0.725514	33.580788	0.750788	17.112242
0.700662	72.736519	0.725935	33.165074	0.751209	16.948634
0.701083	71.743544	0.726357	32.755418	0.751631	16.787712
0.701504	70.766598	0.726778	32.351747	0.752052	16.629442
0.701925	69.805221	0.727199	31.953981	0.752473	16.473792
0.702346	68.858831	0.727620	31.562049	0.752894	16.320735
0.702768	67.926836	0.728042	31.175878	0.753316	16.170244
0.703189	67.008736	0.728463	30.795395	0.753737	16.022290
0.703610	66.104180	0.728884	30.420534	0.754158	15.876842
0.704031	65.212993	0.729305	30.051229	0.754580	15.733878
0.704452	64.335131	0.729726	29.687413	0.755000	15.593370
0.704874	63.470612	0.730148	29.329030	0.755422	15.455289
0.705295	62.619440	0.730569	28.976013	0.755843	15.319611
0.705716	61.781546	0.730990	28.628300	0.756264	15.186312
0.706138	60.956748	0.731412	28.285832	0.756686	15.055365
0.706559	60.144741	0.731833	27.948539	0.757107	14.926745
0.706980	59.345137	0.732254	27.616361	0.757528	14.800427
0.707401	58.557511	0.732675	27.289226	0.757949	14.676390
0.707822	57.781445	0.733096	26.967070	0.758370	14.554604
0.708244	57.016579	0.733518	26.649817	0.758792	14.435049
0.708665	56.262643	0.733939	26.337399	0.759213	14.317700
0.709086	55.519461	0.734360	26.029748	0.759634	14.202535
0.709507	54.786939	0.734781	25.726789	0.760055	14.089525
0.709928	54.065039	0.735202	25.428456	0.760476	13.978650
0.710350	53.353739	0.735624	25.134681	0.760898	13.869889

0.761319	13.763212	0.827303	9.131796	0.879407	8.254076
0.761740	13.658602	0.828171	9.115122	0.880275	8.240906
0.762162	13.556031	0.829040	9.098555	0.881144	8.227776
0.762583	13.455480	0.829908	9.082098	0.882012	8.214683
0.763004	13.356921	0.830777	9.065744	0.882881	8.201624
0.763425	13.260335	0.831645	9.049487	0.883750	8.188601
0.763847	13.165696	0.832514	9.033324	0.884618	8.175613
0.764268	13.072981	0.833382	9.017256	0.885486	8.162658
0.764689	12.982168	0.834251	9.001275	0.886354	8.149744
0.765110	12.893232	0.835119	8.985380	0.887222	8.136876
0.765531	12.806152	0.835988	8.969567	0.888090	8.124066
0.765953	12.720905	0.836856	8.953832	0.888957	8.111312
0.766374	12.637466	0.837725	8.938179	0.889824	8.098599
0.766795	12.555811	0.838594	8.922599	0.890691	8.085844
0.767217	12.475919	0.839462	8.907093	0.891558	8.073063
0.767637	12.397763	0.840330	8.891657	0.892426	8.060259
0.768059	12.321324	0.841199	8.876290	0.893294	8.047499
0.768480	12.246574	0.842068	8.860994	0.894162	8.034776
0.768901	12.173490	0.842936	8.845764	0.895030	8.022094
0.769323	12.102051	0.843805	8.830596	0.895899	8.009442
0.769744	12.032220	0.844673	8.815494	0.896767	7.996819
0.776355	11.127688	0.845542	8.800453	0.897636	7.984219
0.782952	10.534792	0.846410	8.785474	0.898505	7.971643
0.789513	10.148847	0.847279	8.770556	0.899373	7.959088
0.796078	9.886417	0.848147	8.755696	0.900242	7.946554
0.796905	9.855930	0.849016	8.740893	0.901110	7.934038
0.797774	9.828446	0.849885	8.726146	0.901978	7.921546
0.798642	9.801204	0.850753	8.711456	0.902847	7.909069
0.799510	9.774779	0.851621	8.696822	0.903716	7.896614
0.800379	9.749072	0.852490	8.682242	0.904584	7.884177
0.801247	9.724009	0.853358	8.667718	0.905453	7.871756
0.802116	9.699526	0.854227	8.653246	0.906321	7.859355
0.802984	9.675574	0.855096	8.638827	0.907190	7.846971
0.803853	9.652113	0.855964	8.624460	0.908058	7.834605
0.804721	9.629105	0.856833	8.610146	0.908927	7.822255
0.805590	9.606523	0.857701	8.595882	0.909795	7.809923
0.806458	9.584340	0.858570	8.581667	0.910664	7.797609
0.807327	9.562536	0.859438	8.567500	0.911533	7.785311
0.808195	9.541088	0.860307	8.553383	0.912401	7.773034
0.809064	9.519979	0.861175	8.539310	0.913269	7.760778
0.809932	9.499193	0.862044	8.525287	0.914137	7.748546
0.810801	9.478714	0.862912	8.511309	0.915006	7.736340
0.811669	9.458527	0.863781	8.497378	0.915874	7.724179
0.812538	9.438615	0.864649	8.483489	0.916741	7.712041
0.813406	9.418968	0.865518	8.469650	0.917608	7.699977
0.814275	9.399574	0.866387	8.455853	0.918475	7.687847
0.815144	9.380415	0.867255	8.442101	0.919342	7.675775
0.816012	9.361488	0.868124	8.428393	0.920210	7.663580
0.816880	9.342776	0.868992	8.414730	0.921077	7.651466
0.817749	9.324269	0.869861	8.401109	0.921945	7.639315
0.818617	9.305961	0.870729	8.387533	0.922814	7.627230
0.819486	9.287838	0.871598	8.374006	0.923682	7.615155
0.820355	9.269892	0.872466	8.360532	0.924550	7.603122
0.821223	9.252115	0.873333	8.347142	0.925418	7.591106
0.822092	9.234500	0.874201	8.333828	0.926287	7.579120
0.822960	9.217038	0.875067	8.320645	0.927155	7.567153
0.823828	9.199723	0.875935	8.307271	0.928024	7.555215
0.824697	9.182547	0.876802	8.293947	0.928892	7.543298
0.825566	9.165505	0.877670	8.280567	0.929761	7.531410
0.826434	9.148592	0.878538	8.267298	0.930629	7.519545

0.931498	7.507709	0.954915	7.200925	0.978315	6.923268
0.932366	7.495897	0.955782	7.190008	0.979181	6.913687
0.933234	7.484122	0.956650	7.179067	0.980049	6.904031
0.934102	7.472373	0.957517	7.168282	0.980916	6.894524
0.934971	7.460671	0.958385	7.157575	0.981783	6.884985
0.935839	7.448998	0.959252	7.147023	0.982651	6.875570
0.936706	7.437409	0.960118	7.136679	0.983518	6.866158
0.937573	7.425833	0.960983	7.126295	0.984386	6.856866
0.938440	7.414378	0.961849	7.116063	0.985253	6.847588
0.939306	7.402849	0.962715	7.105225	0.986121	6.838438
0.940172	7.391365	0.963582	7.094563	0.986987	6.829293
0.941039	7.379803	0.964450	7.083864	0.987854	6.820248
0.941906	7.368258	0.965318	7.073346	0.988721	6.811182
0.942774	7.356769	0.966186	7.062921	0.989588	6.802151
0.943642	7.345314	0.967054	7.052581	0.990455	6.793145
0.944509	7.333940	0.967922	7.042316	0.991322	6.784171
0.945377	7.322588	0.968790	7.032129	0.992190	6.775281
0.946245	7.311316	0.969657	7.022044	0.993058	6.766433
0.947113	7.300056	0.970523	7.012130	0.993925	6.757680
0.947980	7.288892	0.971387	7.002300	0.994793	6.748971
0.948848	7.277736	0.972251	6.992657	0.995661	6.740349
0.949715	7.266696	0.973116	6.982473	0.996529	6.731764
0.950582	7.255682	0.973981	6.972616	0.997397	6.723260
0.951449	7.244750	0.974848	6.962427	0.998264	6.714777
0.952315	7.233901	0.975714	6.952636	0.999132	6.706372
0.953181	7.222900	0.976581	6.942712	1.000000	6.698002
0.954048	7.212028	0.977448	6.933040		

Step 4: INT3 → TS4 → P + H_2O

Intrinsic Coordinate	Electronic Energy (kJ/mol)	0.033353	1.635385	0.073380	5.017987
		0.034684	1.720214	0.074716	5.171237
		0.036011	1.804228	0.076051	5.327801
		0.037338	1.888706	0.077385	5.487744
		0.038668	1.975852	0.078721	5.651134
0.000000	0.000000	0.040001	2.065518	0.080056	5.818029
0.001334	0.050916	0.041336	2.157216	0.081392	5.988492
0.002668	0.102980	0.042671	2.250789	0.082726	6.162584
0.004004	0.156102	0.044007	2.346220	0.084061	6.340354
0.005339	0.210305	0.045341	2.443537	0.085397	6.521860
0.006675	0.265606	0.046677	2.542781	0.086732	6.707147
0.008010	0.322028	0.048012	2.643994	0.088068	6.896262
0.009344	0.379597	0.049347	2.747226	0.089402	7.089246
0.010680	0.438325	0.050683	2.852530	0.090737	7.286146
0.012015	0.498249	0.052017	2.959955	0.092073	7.486997
0.013351	0.559379	0.053352	3.069559	0.093408	7.691828
0.014685	0.621779	0.054688	3.181400	0.094742	7.900673
0.016020	0.685468	0.056023	3.295535	0.096078	8.113562
0.017355	0.750720	0.057359	3.412029	0.097413	8.330512
0.018687	0.817134	0.058693	3.530946	0.098749	8.551548
0.020020	0.885216	0.060028	3.652346	0.100084	8.776687
0.021349	0.952925	0.061364	3.776299	0.101418	9.005938
0.022679	1.022367	0.062699	3.902871	0.102754	9.239316
0.024011	1.093221	0.064035	4.032130	0.104089	9.476824
0.025345	1.165916	0.065369	4.164145	0.105425	9.718467
0.026680	1.240142	0.066704	4.298986	0.106760	9.964250
0.028014	1.315895	0.068040	4.436720	0.108095	10.214166
0.029350	1.393145	0.069375	4.577415	0.109430	10.468212
0.030685	1.471971	0.070709	4.721145	0.110765	10.726380
0.032020	1.552571	0.072045	4.867979	0.112101	10.988665

0.113436	11.255049	0.193548	33.464166	0.273659	61.858242
0.114771	11.525520	0.194883	33.910806	0.274994	62.339334
0.116106	11.800063	0.196217	34.359044	0.276330	62.820142
0.117441	12.078657	0.197553	34.808845	0.277664	63.300645
0.118777	12.361282	0.198888	35.260166	0.279000	63.780820
0.120111	12.647916	0.200224	35.712973	0.280335	64.260635
0.121447	12.938532	0.201559	36.167226	0.281670	64.740073
0.122782	13.233108	0.202893	36.622887	0.283006	65.219100
0.124117	13.531612	0.204229	37.079918	0.284340	65.697692
0.125453	13.834019	0.205564	37.538283	0.285676	66.175819
0.126787	14.140292	0.206900	37.997945	0.287011	66.653458
0.128123	14.450403	0.208234	38.458862	0.288346	67.130577
0.129458	14.764318	0.209569	38.921005	0.289682	67.607153
0.130793	15.082001	0.210905	39.384333	0.291016	68.083153
0.132129	15.403415	0.212240	39.848807	0.292352	68.558553
0.133463	15.728522	0.213576	40.314395	0.293687	69.033327
0.134799	16.057285	0.214910	40.781059	0.295022	69.507450
0.136134	16.389663	0.216246	41.248766	0.296357	69.980896
0.137469	16.725619	0.217581	41.717473	0.297692	70.453641
0.138805	17.065107	0.218916	42.187151	0.299028	70.925664
0.140139	17.408089	0.220252	42.657759	0.300363	71.396939
0.141475	17.754518	0.221586	43.129262	0.301699	71.867449
0.142810	18.104356	0.222922	43.601626	0.303033	72.337172
0.144145	18.457554	0.224257	44.074815	0.304368	72.806089
0.145480	18.814068	0.225592	44.548791	0.305704	73.274179
0.146815	19.173853	0.226928	45.023521	0.307039	73.741426
0.148151	19.536865	0.228262	45.498967	0.308375	74.207809
0.149486	19.903060	0.229598	45.975096	0.309709	74.673316
0.150822	20.272386	0.230933	46.451871	0.311044	75.137924
0.152156	20.644797	0.232268	46.929256	0.312380	75.601622
0.153491	21.020252	0.233603	47.407217	0.313715	76.064392
0.154827	21.398697	0.234938	47.885720	0.315051	76.526218
0.156162	21.780087	0.236274	48.364727	0.316385	76.987082
0.157498	22.164376	0.237609	48.844206	0.317720	77.446975
0.158832	22.551517	0.238944	49.324126	0.319056	77.905879
0.160167	22.941459	0.240279	49.804449	0.320391	78.363779
0.161503	23.334155	0.241614	50.285141	0.321726	78.820663
0.162838	23.729560	0.242950	50.766174	0.323061	79.276516
0.164174	24.127626	0.244285	51.247510	0.324396	79.731326
0.165508	24.528301	0.245619	51.729124	0.325732	80.185073
0.166843	24.931543	0.246955	52.210979	0.327067	80.637748
0.168179	25.337301	0.248290	52.693050	0.328402	81.089334
0.169514	25.745532	0.249626	53.175302	0.329737	81.539817
0.170849	26.156184	0.250961	53.657711	0.331072	81.989180
0.172184	26.569215	0.252295	54.140246	0.332408	82.437405
0.173519	26.984574	0.253631	54.622882	0.333742	82.884470
0.174855	27.402217	0.254966	55.105590	0.335078	83.330361
0.176190	27.822101	0.256302	55.588349	0.336413	83.775050
0.177525	28.244179	0.257637	56.071131	0.337748	84.218515
0.178860	28.668402	0.258972	56.553911	0.339084	84.660734
0.180196	29.094730	0.260307	57.036669	0.340418	85.101678
0.181531	29.523117	0.261642	57.519383	0.341754	85.541321
0.182865	29.953518	0.262978	58.002026	0.343089	85.979635
0.184201	30.385893	0.264313	58.484583	0.344424	86.416600
0.185536	30.820196	0.265648	58.967031	0.345760	86.852181
0.186872	31.256386	0.266983	59.449346	0.347094	87.286360
0.188207	31.694419	0.268318	59.931511	0.348430	87.719113
0.189541	32.134253	0.269654	60.413506	0.349765	88.150419
0.190877	32.575852	0.270988	60.895306	0.351101	88.580261
0.192212	33.019170	0.272324	61.376891	0.352436	89.008619

0.353770	89.435481	0.433883	111.588423	0.513993	122.553239
0.355106	89.860836	0.435217	111.887717	0.515327	122.518887
0.356441	90.284667	0.436552	112.184346	0.516662	122.470071
0.357777	90.706969	0.437888	112.478295	0.517998	122.406303
0.359111	91.127729	0.439223	112.769549	0.519333	122.326947
0.360446	91.546934	0.440559	113.058094	0.520667	122.231169
0.361782	91.964575	0.441893	113.343919	0.522003	122.117939
0.363117	92.380643	0.443228	113.627001	0.523338	121.986076
0.364453	92.795118	0.444564	113.907325	0.524674	121.834335
0.365787	93.207994	0.445899	114.184867	0.526009	121.661519
0.367122	93.619247	0.447235	114.459599	0.527343	121.466570
0.368458	94.028867	0.448569	114.731488	0.528679	121.248625
0.369793	94.436827	0.449904	115.000492	0.530014	121.006966
0.371129	94.843113	0.451240	115.266565	0.531349	120.740979
0.372463	95.247700	0.452575	115.529645	0.532685	120.450037
0.373798	95.650565	0.453910	115.789662	0.534019	120.133441
0.375134	96.051678	0.455245	116.046530	0.535355	119.790386
0.376469	96.451014	0.456580	116.300156	0.536690	119.419954
0.377805	96.848546	0.457916	116.550429	0.538025	119.021182
0.379139	97.244240	0.459251	116.797232	0.539361	118.593123
0.380474	97.638063	0.460586	117.040429	0.540695	118.134924
0.381810	98.029984	0.461921	117.279896	0.542030	117.645880
0.383145	98.419966	0.463256	117.515500	0.543366	117.125440
0.384481	98.807970	0.464592	117.747122	0.544701	116.573190
0.385815	99.193963	0.465926	117.974648	0.546036	115.988796
0.387150	99.577903	0.467262	118.197988	0.547371	115.371947
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0.392491	101.092470	0.472602	119.048348	0.552712	112.573976
0.393826	101.465656	0.473938	119.250037	0.554047	111.790624
0.395162	101.836613	0.475273	119.447333	0.555382	110.973508
0.396496	102.205317	0.476608	119.640215	0.556718	110.122678
0.397832	102.571763	0.477944	119.828644	0.558052	109.238249
0.399167	102.935938	0.479278	120.012563	0.559388	108.320385
0.400502	103.297843	0.480614	120.191888	0.560723	107.369318
0.401838	103.657471	0.481949	120.366499	0.562058	106.385365
0.403172	104.014827	0.483284	120.536256	0.563394	105.368963
0.404508	104.369913	0.484620	120.700990	0.564728	104.320680
0.405843	104.722733	0.485954	120.860508	0.566063	103.241195
0.407179	105.073285	0.487289	121.014612	0.567399	102.131273
0.408514	105.421573	0.488625	121.163097	0.568734	100.991740
0.409848	105.767595	0.489960	121.305764	0.570070	99.823490
0.411184	106.111344	0.491295	121.442418	0.571404	98.627506
0.412519	106.452809	0.492630	121.572872	0.572739	97.404879
0.413855	106.791979	0.493965	121.696940	0.574075	96.156832
0.415190	107.128836	0.495301	121.814420	0.575410	94.884693
0.416524	107.463361	0.496636	121.925101	0.576746	93.589852
0.417860	107.795529	0.497971	122.028729	0.578080	92.273702
0.419195	108.125315	0.499306	122.125012	0.579415	90.937582
0.420531	108.452694	0.500641	122.213591	0.580751	89.582779
0.421866	108.777637	0.501977	122.294047	0.582086	88.210622
0.423200	109.100119	0.503311	122.365878	0.583421	86.822610
0.424536	109.420110	0.504646	122.428517	0.584756	85.420532
0.425871	109.737588	0.505982	122.481318	0.586091	84.006451
0.427207	110.052527	0.507317	122.523592	0.587427	82.582545
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0.600779	68.232872	0.680889	13.075725	0.761000	-15.402133
0.602113	66.831236	0.682223	12.484098	0.762335	-15.781615
0.603449	65.442971	0.683558	11.898314	0.763671	-16.158419
0.604784	64.069824	0.684894	11.318011	0.765005	-16.532574
0.606119	62.713636	0.686229	10.742858	0.766340	-16.904106
0.607455	61.376072	0.687565	10.172584	0.767676	-17.273049
0.608789	60.058391	0.688899	9.606964	0.769011	-17.639430
0.610125	58.761315	0.690234	9.045835	0.770346	-18.003282
0.611460	57.485168	0.691570	8.489090	0.771681	-18.364632
0.612795	56.230142	0.692905	7.936663	0.773017	-18.723512
0.614131	54.996606	0.694241	7.388530	0.774352	-19.079950
0.615465	53.785218	0.695575	6.844689	0.775687	-19.433967
0.616800	52.596825	0.696910	6.305157	0.777022	-19.785595
0.618136	51.432132	0.698246	5.769954	0.778357	-20.134854
0.619471	50.291334	0.699581	5.239091	0.779693	-20.481770
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0.628816	42.879698	0.708927	1.643568	0.789038	-22.846048
0.630152	41.889868	0.710262	1.146530	0.790374	-23.174829
0.631487	40.916792	0.711598	0.653395	0.791709	-23.501404
0.632822	39.960664	0.712933	0.164054	0.793045	-23.825796
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0.651514	27.975537	0.731626	-6.339435	0.811737	-28.148030
0.652849	27.205297	0.732960	-6.781525	0.813073	-28.441999
0.654185	26.446730	0.734296	-7.220750	0.814407	-28.734120
0.655520	25.699407	0.735631	-7.657111	0.815743	-29.024406
0.656854	24.962726	0.736967	-8.090596	0.817078	-29.312875
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0.660861	22.809593	0.740972	-9.373781	0.821083	-30.167475
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0.663530	21.415442	0.743643	-10.214799	0.823754	-30.728269
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0.903866	-44.486808				
0.905201	-44.671457				

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