**Electronic Structure: Determination of Reaction Mechanism**

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**ABSTRACT**

The goal of this experiment was to determine the reaction mechanism by which a dehydration reaction occurs. The two proposed mechanisms for this reaction were an E1 elimination mechanism and an E2 elimination mechanism. In order to determine which of the two elimination mechanisms was thermodynamically favored, the overall change in internal energy, enthalpy, free energy, and entropy for each of the mechanisms was calculated. However, calculations for both the E1 and E2 elimination mechanisms resulted in the exact same values for ΔU, ΔG, ΔH, and ΔS. Therefore, further inquiry was necessary in order to determine which mechanism was more likely. To deduce which mechanism was more thermodynamically favorable, each individual step was designated as being enthalpically or entropically driven, as well as being spontaneous or nonspontaneous. This allowed us to conclude that the E2 mechanism was more thermodynamically likely, contrary to what we’d expect from an organic chemistry standpoint. Additionally, it was concluded that the dehydration reaction was entropically driven due to the fact that, for the overall reaction, the entropy—as opposed to the enthalpy—was pushing the reaction towards spontaneity. All thermodynamic data was computed using the Gaussian 16 software.



**INTRODUCTION**

The overall reaction studied in this paper, shown in **Figure 1**, is a dehydration reaction. The purpose of this experiment was to determine the most likely reaction mechanism via which this dehydration reaction occurs. Simply put, a dehydration reaction is a reaction in which a hydroxyl group becomes protonated, thus allowing the loss of a water molecule and resulting in a pi bond [4].

**Overall Reaction**



**Molecule 2**

**Molecule 1**

***Figure 1.*** *Overall reaction scheme for the proposed dehydration reaction.*

The two proposed mechanisms for this reaction are both elimination reactions. Mechanism 1, the first of the proposed mechanisms, is an E1 elimination mechanism. Mechanism 2, the second of the proposed mechanisms, is an E2 elimination mechanism. Mechanisms 1 and 2 are shown below in **Figure 2** and **Figure 3**, respectively.



**Step A1**

**Molecule 2**

**Molecule 4**

**Step D**

**Step C**

**Step B**

**Molecule 3**

**Molecule 1**

***Figure 2.*** *Mechanism 1: A proposed mechanism which occurs via an E1 elimination mechanism.*



**Molecule 1**

**Step A2**

**Step F**

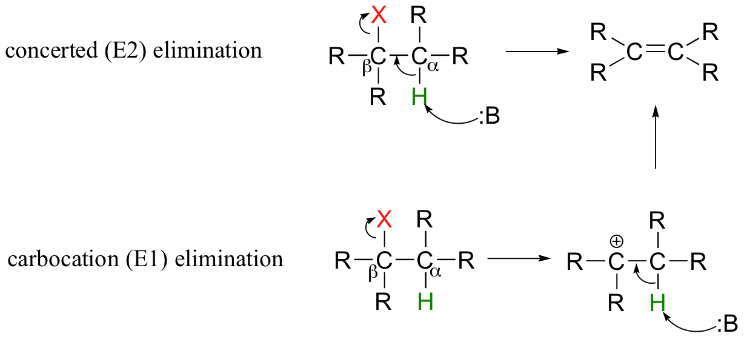
**Step E**

**Molecule 2**

**Molecule 3**

***Figure 3.*** *Mechanism 2: A proposed mechanism which occurs via an E2 elimination mechanism.*

Elimination reactions can occur via an E1 mechanism or an E2 mechanism. An E1 mechanism is a two step process, in which the first step involves the loss of the leaving group and the second step involves deprotonation via a base and the formation of a pi bond [1]. An E2 mechanism, on the other hand, is a one step process in which a base pulls off a proton from the substrate, leading to a shift in electrons, which results in the formation of a pi bond and the loss of a leaving group [1]. A basic reaction scheme detailing the two mechanisms is shown below in **Figure 4**.



***Figure 4****. Basic reaction scheme for E1 and E2 elimination reactions [5]*.

There are important differences to note between an E1 and an E2 reaction. With an E1 reaction, there is no need for a strong base, nor is there a requirement regarding the stereochemistry of the substrate. However, with an E2 mechanism, a strong base is necessary in order to occur, and there is a stereochemical requirement in that the leaving group must be *anti* to the hydrogen removed [1].

In the context of the two proposed mechanisms, both have water acting as the base. Therefore, through the lens of organic chemistry, the E1 mechanism is more likely to occur because water is a weak base, and thus is very unlikely to cause an E2 mechanism to occur.

Other aspects of chemistry which are significant to this experiment are thermodynamic state functions. The state functions of interest to this paper include internal energy (U), Gibb’s free energy (G), enthalpy (H), and entropy (S). If values for the Gibb’s free energy, enthalpy, and entropy are known for a given reaction, it can be determined whether the reaction is enthalpically or entropically driven. When a reaction has ΔH>>-TΔS, where T is the temperature, then the reaction is enthalpically driven [3]. On the other hand, when a reaction has -TΔS>>ΔH, the reaction is entropically driven [3].

**METHODS**

The goal of this experiment was to determine which of the two elimination mechanisms, E1 or E2, was more likely by comparing their respective changes in internal energy, free energy, enthalpy, and entropy. The thermodynamic values were all computed using the GaussView program, Version 16 [2].

To begin, each of the six molecules involved with the reaction mechanisms (**Molecules 1-4**, **H3O+**, and **H2O**) were built within the program. Once a molecule was built within the program, the respective molecule now had an input file to work with. The next step for a given molecule was then to set up calculation parameters and run the calculation. For each molecule, three different types of calculation jobs were run: first, geometry optimization; then, a series of energy calculations; lastly, an optimization and frequency calculation.

When setting up calculation parameters, one first has to select the job type. As mentioned, the first job was a geometry optimization for the molecule. After the job type is chosen, one then has to select a method and basis set. For the geometry optimization step, the method was Hartree-Fock and the basis set chosen was the lowest basis set of 3-21G. For the first geometry step, these were the only parameters chosen, and the calculation was then run.

For the subsequent energy calculations, the job type was an energy calculation, the method chosen was Density Functional Theory (DFT), and the basis set was started off at 3-21G. The basis sets were then slowly built up per calculation, in the following manner: DFT 6-31G, DFT 6-311G, DFT 6-311G (2d), and DFT 6-311G (2d,2p).

For the final optimization and frequency calculation, the job type was an Opt/Freq calculation, the method chosen was DFT, and the basis set was DFT 6-311G (2d,2p). An additional parameter set, for both the energy calculations and the optimization and frequency calculation, was the level of theory, which was set as B3LYP.

These calculation parameters and calculations were run for all six molecules.

**RESULTS AND DISCUSSION**

***Table 1.*** *Thermodynamic data obtained directly via Opt/Freq calculations using the Gaussian software.*

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Thermodynamic Data | Molecule 1 | Molecule 2 | Molecule 3 | Molecule 4 | H3O+ | H2O | Units |
| Basis Set | 6-311G (2d,2p) | 6-311G (2d,2p) | 6-311G (2d,2p) | 6-311G (2d,2p) | 6-311G (2d,2p) | 6-311G (2d,2p) |  |
| E (RB3LYP) | -619.9608 | -543.3953 | -620.3624 | -543.8859 | -76.8567 | -76.4584 | **Hartree** |
| Electronic Energy (EE) | -619.9608 | -543.3953 | -620.3624 | -543.8859 | -76.8567 | -76.4584 | **Hartree** |
| Heat Capacity (Cv) | 56.2910 | 50.9450 | 57.6570 | 52.4090 | 6.4170 | 6.0040 | **cal/mol-K** |
| Entropy (S) | 114.4590 | 104.8640 | 112.2140 | 107.4220 | 46.1010 | 45.0980 | **cal/mol-K** |
| E (Thermal) | 199.2100 | 179.6970 | 207.7690 | 187.9540 | 23.8130 | 15.1370 | **kcal/mol** |
| Dipole Moment | 2.6864 | 6.1623 | 11.4163 | 7.0810 | 1.7809 | 2.1300 | **Debye** |

After building up our basis sets and obtaining the thermodynamic data for the final Opt/Freq calculations for every molecule involved with Mechanisms 1 and 2, the data was compiled and put together as shown in **Table 1**. As can be observed in the table, the larger and more complex **Molecules 1-4** have significantly larger electronic energy, entropy, and thermal energy values as compared to the simpler and less complex **H2O** and **H3O+** molecules. Additionally, it was noted that the duration for the calculations to reach completion—especially the Opt/Freq calculations—were significantly longer for the larger molecules than for the smaller water and hydronium molecules.

***Table 2.*** *Calculated values for changes in free energy (ΔG), internal energy (ΔU), enthalpy (ΔH), and entropy (ΔS) for all steps.*

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Thermodynamic Calculations | Step A1 | Step A2 | Step B | Step C | Step D | Step E | Step F | Overall Rxn | Units |
| ΔG | 52.8551 | 52.8551 | -1.2155 | -4.7804 | 58.8509 | -1.2155 | 54.0706 | 52.8551 | **kcal/mol** |
| ΔU | 62.8475 | 62.8475 | -2.1844 | 6.6447 | 58.3872 | -2.1844 | 65.0319 | 62.8475 | **kcal/mol** |
| ΔH | 63.4399 | 63.4399 | -2.1844 | 7.2371 | 58.3872 | -2.1844 | 65.6243 | 63.4399 | **kcal/mol** |
| ΔS | 35.5030 | 35.5030 | -3.2480 | 40.3060 | -1.5550 | -3.2480 | 38.7510 | 35.5030 | **cal/mol-K** |

**Step A1** is the overall reaction for Mechanism 1, and **Step A2** is the overall reaction for Mechanism 2. In **Table 2**, it is shown that both of these elimination mechanisms have the exact same changes in free energy (ΔG), internal energy (ΔU), enthalpy (ΔH), and entropy (ΔS). Additionally, both of these steps also had the exact same calculated values as the **Overall Rxn**. This observation makes sense, since both the E1 and E2 mechanisms have the same net reaction, when compared to each other as well as when compared to the overall proposed dehydration reaction. Since the values for ΔG, ΔU, ΔH, and ΔS for both Mechanisms 1 and 2 were calculated using all steps per respective mechanism, this suggests that neither mechanism is more thermodynamically favored as compared to the other. If one were to consider which mechanism was more likely to occur, in terms of which had the least energy and was therefore most favorable, both Mechanism 1 and Mechanism 2 would be equally likely since they have the exact same energies.

Therefore, considering this data alone, the paper so far finds it inconclusive as to whether one mechanism is thermodynamically preferable to the other. Since this data alone is inconclusive, each step per mechanism was further analyzed as to whether it was driven by enthalpy or entropy, and as to whether the step was spontaneous or nonspontaneous, as discussed below.

***Table 3.*** *Determination of enthalpically or entropically driven steps, for every individual step.*

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Calculation Section | TΔS (cal/mol-K) | ΔH (cal/mol) | ΔG | Driven By: | Likelihood of Spontaneity |
| Step A1 | 10585.2195 | 63439.9049 | 52854.6854 | Entropy | Spont. at High T |
| Step A2 | 10585.2195 | 63439.9049 | 52854.6854 | Entropy | Spont. at High T |
| Step B | -968.3912 | -2184.3588 | -1215.9676 | Enthalpy | Spont. at Low T |
| Step C | 12017.2339 | 7237.0613 | -4780.1726 | Entropy | Spont. at High T |
| Step D | -463.6232 | 58387.2024 | 58850.8257 | Entropy | Never Spontaneous |
| Step E | -968.3912 | -2184.3588 | -1215.9676 | Enthalpy | Spont. at Low T |
| Step F | 11553.6107 | 65624.2637 | 54070.6531 | Entropy | Spont. at High T |
| Overall Rxn | 10585.2195 | 63439.9049 | 52854.6854 | Entropy | Spont. at High T |

As mentioned in the introduction, a reaction will be enthalpically driven when ΔH>>-TΔS and it will be entropically driven when -TΔS>>ΔH [3]. As shown in **Table 3** above, values for TΔS, ΔH, and ΔG were calculated for all steps for both Mechanisms 1 and 2, as well as for the overall reaction. Using this data, all steps were then designated as being enthalpically or entropically driven. Additionally, it was indicated whether the respective step would be spontaneous or nonspontaneous, and under which conditions. For the overall dehydration mechanism, it was determined that the reaction was entropically driven due to the fact that the entropy—as opposed to the enthalpy—was pushing the reaction towards spontaneity [6].

As shown in **Table 3**, it was concluded that **Step D** was a step which would be nonspontaneous at all temperatures. This is because the value for entropy is negative and the value for enthalpy is positive, leading to a value for Gibbs Free Energy that will always be positive, regardless of temperature [6]. Therefore, the reaction for Step D would not go forward without an energy contribution from an outside force. Since this step is part of Mechanism 1, we concluded that considering this data, Mechanism 1 would not be thermodynamically favored. Instead, Mechanism 2 would be the more likely mechanism for the dehydration reaction, since the E2 elimination mechanism does *not* have any nonspontaneous step for all temperatures. Mechanism 1 would be the less likely mechanism for the reaction due to the fact that energy would be needed from an outside force in order to proceed.

However, in the real world, there would be interactions between the molecules of the reaction and the molecules of solvent, in this case being water. Thus, these real-world interactions between the molecule and the water—and resultant hydrogen bonding—would help provide the energy necessary to push the reaction forward. These real-world interactions which could help the reaction actually happen in the real world are missing in the Gaussian program, where the simulation is simply run in a gas phase that acts like water.

**CONCLUSION**

Based off of the thermodynamic data shown in **Table 2,** it was presumed that both Mechanism 1 and Mechanism 2 are equally likely because all calculated ΔG, ΔU, ΔH, and ΔS values are exactly the same, when compared to each other and when compared to the overall reaction. However, after considering the -TΔS and the ΔH values and the likelihood of spontaneity, as shown in **Table 3**, it was concluded that Mechanism 2 would actually be the more thermodynamically favored mechanism, since this mechanism does *not* have any steps that are nonspontaneous at all temperatures. In short, the E2 elimination mechanism is more thermodynamically favored, according to our findings.

However, based off of our knowledge of organic chemistry, we know that an E1 mechanism would be more likely for this dehydration reaction due to the fact that water is not a strong base. An E2 mechanism needs a strong base, which is absent in the proposed dehydration mechanism, and therefore our knowledge of organic chemistry contradicts with our thermodynamic conclusion.

Additionally, the dehydration reaction was determined to be entropically driven. This is due to the fact that for the overall reaction, the entropy—as opposed to the enthalpy—was pushing the reaction towards spontaneity.

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**SUPPLEMENTAL INFORMATION**

Molecules Created in Gaussian Software, Version 16

|  |  |  |  |
| --- | --- | --- | --- |
| **Molecule** | | **Molecule** | |
| Molecule 1 |  | Molecule 2 |  |
| Molecule 3 |  | Molecule 4 |  |
| H2O |  | H3O+ |  |