Deanna Patti

Organic vs. Thermodynamic

Determination of a favorable reaction mechanism

**Abstract**

This report used electronic structure calculations to compare two mechanisms of the same overall reaction, Figure 1, and identify their change in free energy in order to determine which is the most likely in terms of thermodynamics. The group proposing the mechanisms used knowledge of E1 and E2 mechanisms to support their reasoning that the first mechanism is more likely. Through thermodynamic calculations of free energy, enthalpy, and entropy, it was found that Mechanism 2 would be more likely to occur. This result disagreed with the group’s proposal that Mechanism 1 would be more likely. Computational errors could have been a possible source of error within the thermodynamic data.

A close up of a clock

Description automatically generated

*Figure 1 – This figure shows the overall reaction the group was analyzing*

**Introduction**

A close up of a clock

Description automatically generated The group proposing the mechanisms used their knowledge of E1 and E2 mechanisms to draw the conclusion that the first mechanism is favorable. An E1 reaction, or unimolecular reaction, involves the deprotonation of a hydrogen nearby, and the carbocation resulting in an alkene product [1]. E2 reactions occur in one single step with one transition state [2]. By examining mechanism one which can be seen in Figure 2, it can be seen in step D that the Hydrogen is deprotonated and the double bond forms in the final molecule. This is one simple way to categorizes Mechanism 1 as an E1 mechanism. A simple way to identify Mechanism 2 as an E2 mechanism is just to note that it occurs in one step. The group made their final conclusion that the E1 mechanism, or Mechanism 1 is more likely because secondary alcohols dehydrate by an E1 mechanism and not an E2. This is because water is not a strong base which would be required for an E2 mechanism.

A close up of a clock

Description automatically generated

*Figure 2 – This figure depicts Figure 3 – This figure depicts*

*Mechanism 1 from the overall Mechanism 2 from the overall reaction. reaction.*

The intention of this paper was to examine the same mechanisms as the group but focus on the thermodynamic properties and determine which would be more likely thermodynamically. The calculations focused on free energy, enthalpy, and entropy which together relate in the Gibbs Relationship:

(1)

We focused on the internal energy as well, however this value was not used in the determination of which mechanism was favorable. The free energy of the reactions was the main insight into determining which of the two mechanisms was thermodynamically favorable. When is less than 0 the forward reaction is considered thermodynamically favored. Conversely, if is greater than 0 the forward reaction is considered thermodynamically unfavorable [3]. The enthalpy and entropy values in the Gibb’s relationship directly influence the and can also indicate the thermodynamic favorability. If is negative while is positive, the reaction is always favorable [3]. If is positive while is negative, the reaction is always unfavorable [3]. If and are both the same sign, the reaction’s favorability is dependent on the temperature [3].

With the focus of this paper being on using computational methods to find thermodynamic values of the two mechanisms, the molecules for both Mechanism 1 and 2 had to be created on GaussView and run through the software to gain the appropriate data for the change in free energy, enthalpy, entropy, and internal energy. GaussView allows you to build or import the molecular structures that interest you, and then set up, launch, monitor and control your Gaussian calculations [4]. The software allows you to set up your own calculations, and once all of your specifically chosen parameters are set up, the reaction will run [4].

**Computational Methods**

The molecules were built using GaussView’s building features, and then ensured proper symmetry and structural parameters. GaussView allows for a molecule to be “cleaned” by the geometry to match proper chemical rules [4]. Along with the main 4 molecules, H2O and H3O+ were also built. Once the molecules were created, and cleaned, they were run through the software with standard temperature and pressure settings. This is how the data was obtained in order to do the thermodynamic calculations.

To explain how the calculations were done, Equation (2) below shows the process of finding the Free Energy of Step C in the first mechanism. In this step, Molecule 3 and H2O were the products and Molecule 1 and H3O+ were the reactants. We used this process of subtracting the products minus the reactants for each step of the mechanisms across the entire table. This includes finding the values for entropy, enthalpy, and internal energy. In order to keep the units consistent, all the values were multiplied by a conversion factor to get the answers in kcal/mol. This conversion factor was a value of 627.509.

(2)

Once all the data was collected and the calculations were complete, each step for Mechanisms 1 and 2 was analyzed to see which were enthalpically driven and which were entropically driven. This was determined by following the rule that if was greater than the value it is enthalpically driven, and if was less than the value it was entropically driven.

**Results and Discussion**

A screenshot of a cell phone screen with text

Description automatically generated Excel was used to calculate all of the values for the thermodynamic values. Figure 4 depicts the 5 different values found from the calculations that were done in order to have enough information to compare the mechanisms thermodynamically and relate them to the Gibbs relation. It can be seen in this figure that for both mechanisms Step A for each was the same in all thermodynamic values. This also lined up for the second steps of each mechanism, which for Mechanism 1 would be step B and for Mechanism 2 be step E. The difference between the reactions that show in the calculations comes in steps C, D, and F because Mechanism 1 has an extra step before reaching the final product.

*Figure 4 – This figure depicts the Excel table created with all of the calculated values for . The steps of these calculations are the same as the steps labeled in Figures 2 and 3 for the mechanisms.*

As mentioned in the above section, each step of both mechanisms was determined to be either enthalpically or entropically driven. Figure 5 below shows the results. Step C in Mechanism 1 was the only step determined to be entropically driven. This is one of the two extra steps in the reaction that Mechanism 1 has over Mechanism 2.

A screenshot of a cell phone

Description automatically generated

*Figure 5 – This figure shows each of the steps of both Mechanisms 1 and 2 and whether they are enthalpically or entropically driven.*

The two reactions free energy changes were plotted against their reaction coordinates to show the difference in reaction rates for each step. Figure 6 shows this plot, and it can be seen that the blue curve depicting Mechanism 1 has a much bigger change in free energy than the red curve depicting Mechanism 2. This signifies that Mechanism 1 is more unlikely than Mechanism 2. This result disagrees with the groups original assumption of Mechanism 1 being more favorable.

A picture containing text

Description automatically generated

*Figure 6 – This figure shows the plot of each mechanism’s change in free energy versus the reaction coordinate. Series 1 in blue is Mechanism 1 and Series 2 in red is Mechanism 2.*

The difference in result from the original group could be due to computational errors either in excel or building errors in GaussView when creating the molecules for the mechanisms. The thermodynamic result will not always be different than the groups in every case, but this happened to be an example of the results being different.

**Conclusion**

The purpose of this report was to use electronic structure calculations to compare the thermodynamics of two mechanisms and determine which was the most likely in terms of thermodynamics. By using GaussView to build the molecules and Excel to run the calculations for the free energy, enthalpy, and entropy for both mechanisms, the two were able to be compared and the more likely mechanism was chosen. While the original group used knowledge of E1 and E2 mechanisms to support their answer that the first mechanism (Figure 2) was more favorable, it was found in the thermodynamic calculations that mechanism 2 (Figure 2) was the more favorable reaction. Acknowledging the possible errors that could have occurred computationally, this does present the possibility that while some reasoning and methods show one reaction to be more likely, a different approach or way of calculating may show other results.

**References:**

[1] Balasubramanian, S. (2019, June 5). E1 Reactions. Retrieved November 14, 2019, from <https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Supplemental_Modules_(Organic_Chemistry)/Reactions/Elimination_Reactions/E1_Reactions>.

[2] Libretexts. (2019, June 5). E2 Reactions. Retrieved November 14, 2019, from <https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Supplemental_Modules_(Organic_Chemistry)/Reactions/Elimination_Reactions/E2_Reactions>.

[3] Enduring Understanding 5.E.2: Gibbs Free Energy. (n.d.). Retrieved November 14, 2019, from <http://www.softschools.com/notes/ap_chemistry/gibbs_free_energy/>.

[4] Using GaussView 6. (n.d.). Retrieved from <https://gaussian.com/gv6main/>.

[5] **Software**: GaussView, Version 16, Dennington, Roy; Keith, Todd A.; Millam, John M. Semichem Inc., Shawnee Mission, KS, 2016.