**Determination of Alcohol Dehydration Mechanism Favorability with Thermodynamic Computation by Gaussian 16**

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**Abstract:** Using the Gaussian 16 electronic structure program, two mechanisms of alcohol dehydration were studied to determine which one is more thermodynamically favored. Because overall reactions would yield the same thermodynamic values, each individual step was modeled and examined to determine favorability based on spontaneity. It was determined that the second reaction, E2, was more favorable due to having less dependence on temperature.



Mechanism Mechanism

**Introduction:**

The Gaussian electronic structure program can be used for simulated analysis of chemical species, allowing computation of thermodynamic values such as enthalpy and entropy. These computations can be performed on the components of an alcohol dehydration to determine if the reaction undergoes an E1 or E2 mechanism.

(1) ΔGo = ΔHo − TΔSo

The overall reactions should have the same thermodynamics regardless of mechanism, so the likely elimination will be verified by analyzing the different steps involved with each one. The likeliness of the mechanism will be based on the spontaneity of the reactions, which is defined by the ΔG value. If negative the reaction is spontaneous, if positive the reaction is not spontaneous.

To ensure accurate values and efficient use of time, the computations will be performed by building up data sets starting with 3-21G, 6-31G to 6-311G.

**Computational Details:**

Using Gaussian, models of each molecule in the reactions were created and analyzed to acquire thermodynamic values. Each molecule was optimized using the Hartree-Fock method with the 3-21G basis set. With this foundation, energy calculations were performed using the DFT method with the 3-21G basis set. The basis sets were then compounded and built up going from 3-21G to 6-31G and ultimately 6-311G. Once the final energy calculation was completed, an Opt+Freq calculation was performed using DFT with the 6-311G basis set. The thermodynamics of each of the steps were then calculated using the [products – reactants] formula for each measurement. The models were analyzed at 298 K and with default solvent settings.

**Results and Discussion:**

For the first mechanism, the results in Figure 1 show that Step 1 is not spontaneous while Steps 2 and 3 are spontaneous. The first two steps are entropically driven as temperature increases, while the third step is enthalpically driven. It should be noted that 1 and 2 require high temperatures to maintain spontaneity, while 3 requires low temperatures.

For the second mechanism, the data in Figure 2 show that Step 1 is only spontaneous when temperatures are high, as in mechanism 1, however Step 2 is negative at all temperatures. Step 1 is once again entropically driven, due to being the same Step as the first mechanism, and Step 2 is favored by both the entropy and enthalpy terms.

**(1)**

|  |  |  |  |
| --- | --- | --- | --- |
| **Mechanism 1** | Δ**H** | Δ**S** | Δ**G** |
| Step 1 | 0.9488 | 0.000481 | 0.8051 |
| Step 2 | 9.258 | 0.0406 | -2.849 |
| Step 3 | -742.037 | -0.00088 | -741.77 |

**(2)**

|  |  |  |  |
| --- | --- | --- | --- |
| **Mechanism 2** | Δ**H** | Δ**S** | Δ**G** |
| Step 1 | 0.9488 | 0.000481 | 0.8051 |
| Step 2 | -732.778 | 0.0397 | -744.623 |

**Figures 1 & 2**. Thermodynamic values of Mechanisms 1 and 2 as obtained from Gaussian. These values were ultimately collected after compiling calculations while building up basis sets in Gaussian 16. Values are in kcal\*mol-1 (ΔH and ΔG) and kcal\*mol-1K-1 (ΔS)

The changes in thermodynamic values of the overall reactions of each mechanism are not included in the tables. They were omitted because they produce equivalent values due to the starting reactants and final products being identical in both.

When comparing the two mechanisms, the data suggests that mechanism 2 is more thermodynamically favored. While mechanism 1 has two spontaneous steps and one non-spontaneous step, the spontaneity is dependent on the temperature the reaction occurs at. If the temperature were reduced, the first two steps would become non-spontaneous. Mechanism 2 is less dependent on temperature because it’s Step 2 is always spontaneous due to the negative ΔH and ΔS values.

**Conclusion:**

Although the anticipated result was for mechanism 1 to be more thermodynamically favorable than mechanism 2, the data collected suggests the opposite. Overall, the two pathways have the same changes in enthalpy, entropy, Gibbs free energy and internal energy but the individual steps exhibit behaviors that vary based on temperature. Each of the steps could be manipulated by changing the temperatures but mechanism 2 requires less manipulation due to its second step being spontaneous at any temperature, a characteristic that none of the mechanism 1 steps possess.

**Bibliography:**

(1) Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

(2) Format

https://pubs.acs.org/doi/pdf/10.1021/ja8025906

(3) Spontaneous Reactions and Free Energy https://chem.libretexts.org/Courses/University\_of\_Kentucky/UK%3A\_CHE\_103\_-\_Chemistry\_for\_Allied\_Health\_(Soult)/Chapters/Chapter\_11%3A\_Properties\_of\_Reactions/11.5%3A\_Spontaneous\_Reactions\_and\_Free\_Energy