Vinylidene isomerization: A computational study

Abstract

Vinylidene is a biradical that is very high in energy relative to acetylene with a 45.91 kcal/mole energy difference and a low barrier to isomerization. Thus, vinylidene isomerizes to acetylene. To develop a better understanding of the isomerization mechanism of vinylidene to acetylene, the dynamics were studied using computational methods. First, the formation of vinylidene was carried by subjecting vinylbromide to vacuum UV radiation of a wavelength of 193 nm. Next, the experimental energy transfer amounts were obtained from the examination of the time-resolved IR emission and using the Lennard-Jones collision rate parameters obtained by our group. Analysis of the data showed a loss of energy resulting from the collisions of different inert gas atoms with acetylene. Vinylidene showed tremendous enhancement of energy transfer per collision rate when its vibrational energy was higher than 1.5 x 10^4 cm^-1. This energy is near the barrier of its isomerization to vinylidene. In order to test the reproducibility of the results, a new set of parameters was developed from high-level ab-initio (CCSD(T)/CBS/aug-cc-pVQZ) computations in collaboration with Bill Hase and colleagues from Texas Tech University. The previous parameters were for the more flexible exponential equation. The classical trajectories were only obtained for the non-bonding interactions of Ar with acetylene. The classical trajectories were compared to the experimental energy transfer amounts obtained by the computational program Venus 96. The results obtained were compared with the IR spectra generated by the emissions of the excited molecules. Based on the analysis of the spectra, sequential ordered vibrational energies were generated for the excited molecules. The results obtained show that the amount of transferred energy increases as the vibrational energy of acetylene increases. Thus, the pre-exponential parameters are valid since they are in agreement with the experimental results.

Introduction

The isomerization of vinylidene to acetylene has gained the attention of chemists in spite of the molecular simplicity of its reacting species. Vinylidene is a highly energized biradical relative to acetylene with a 45.91 kcal/mole energy difference and a low barrier (~4.5 kcal/mole) to isomerization. The importance of this reaction lies in its dynamics that provide a key example for isomerization reactions that involve reactants of higher complexity.

Recent studies have introduced more accurate results and new trends in the mechanism by relying on technologically advanced experimental and computational methods. Bittner and Köppel showed that the lifetime of vinylidene increases as the vibrational excitation of the acetylene-vinylidene rearrangement decreases implying a longer lifetime for vinylidene at lower excitation energies than what have been previously reported in the literature. Moreover, the experimental results provided by our group showed that vinylidene revisits acetylene more frequently than expected at higher energies prior to relaxation. The results support and provide a reason for the longer life span of vinylidene reported by Schork and Köppel which has exceeded the values documented in the literature.

In order to develop a better understanding of the mechanism, we focused on the energy-transfer aspect of the acetylene-vinylidene isomerization mechanism. Thus, computational methods were undertaken to mimic the conditions of the system with changes in its energy due to interactions with other chemical species present. The results obtained were compared with the IR spectra generated by the emissions of the excited molecules. Based on the analysis of the spectra, sequentially ordered models were constructed to represent the chemical changes experienced by the reactant as a function of time.

The models shed light on the dynamics of the mechanism. However, the energy transfer per collision with an inert gas needs to be examined since it is related to the vibrational energy of the molecule. Moreover, the reproducibility of the results is yet to be tested in order to verify their validity and exclude systematic error. Thus, different sets of parameters for the Lennard-Jones and an exponential potential function are to be produced to describe the non-bonding interactions of the reactant with the inert gas atoms present in the system.

Materials and Methods

The experimental results modeled in the computations were carried out as follows. The formation of vinylidene was carried by subjecting vinylbromide to vacuum UV radiation of a wavelength of 193 nm as shown in the reaction presented in Figure 1. The process led to the formation of vinylidene with HBr as a byproduct. Each of these excited molecules experienced energy transfer that resulted in a loss of energy as well as emission of IR which was measured in the experiment.

Results and Discussion

The results presented in Figures 3 through 5 show that the Lennard-Jones potentials used in the previous work are of lower quality compared to the results from the new parameters for the more flexible exponential equation. The new results provide a more accurate description for the intermolecular interactions between the interacting atoms. Analysis of the data presented in Figures 6 and 7 showed a loss of energy resulting from the collisions of different inert gas atoms with acetylene. Acetylene had tremendous enhancement of energy transfer per collision rate when its vibrational energy was higher than 1.5 x 10^4 cm^-1. This energy is near the barrier of its isomerization to vinylidene. Moreover, the amount of vibrational energy lost by acetylene per collision with an ideal gas atom simplified as the vibrational energy of acetylene increased.

Conclusion

The transfer energy amounts obtained by the classical trajectories that were generated by the pre-exponential parameters showed that the amount of transferred energy increases as the vibrational energy of acetylene increases. Thus, the pre-exponential parameters are valid since they are in agreement with the experimental results.

References

4. The diagrams of vinylidene in orientations A, B, and C presented in Figures 3 through 5 are reprinted with permission from Emilio Martinez Nuñez.