Computational Study of the Photochemical Fragmentation of Hydantoin

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http://dx.doi.org/10.5772/intechopen.74312

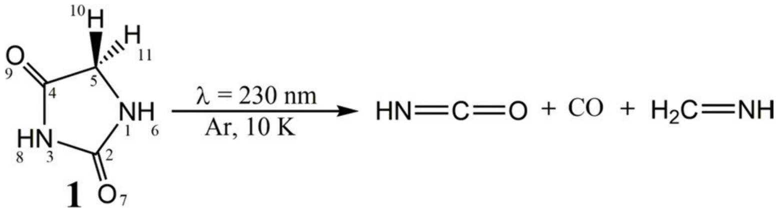
Abstract

The mechanism of the photochemical fragmentation reaction is investigated theoretically using the model system, hydantoin, using the CAS(22,16)/6-31G(d) and MP2-CAS-(22,16)/6-311G(d)//CAS(22,16)/6-31G(d) methods. The model investigation demonstrates that the preferred reaction route for the photofragmentation reaction is as follows: hydantoin → Franck-Condon region → conical intersection → fragment photoproducts (i.e., CO, isocyanic acid, and methylenimine). The theoretical finding additionally suggests that no organic radicals exist during the fragmentation reaction. Moreover, due to the high activation energy, the theoretical evidences suggest that it would be difficult to yield the three fragments under the thermal reaction. All the above theoretical observations are consistent with the available experimental results.

Keywords: hydantoin, 2,4-imidazolidinediones, photofragmentation, conical intersection, CASSCF

1. Introduction

Hydantoins (or 2,4-imidazolidinediones, **1**) are known to be useful chemicals in various pharmaceutical and agrochemical fields [1]. In order to examine the electronic structure, infrared spectrum, and unimolecular UV-induced photochemistry of the parent hydantoin monomer, Ildiz and co-workers recently reported that upon irradiation at $\lambda = 230$ nm, photochemical transformation of matrix-isolated **1** took place leading to formation of CO, isocyanic acid, and methylenimine (**Scheme 1**) [2]. However, since then neither experimental nor theoretical work has been devoted to the study of the photofragmentation mechanism of such five-membered ring heterocyclic molecule. In order to obtain more understanding of the photochemical



Scheme 1. The experimental result. See ref. [2].

behaviors of the transformation of hydantoin and their related heterocyclics to various photoproducts, the potential energy surfaces on its both singlet ground state and singlet excited state were investigated by CASSCF and MP2-CAS calculations. It will be shown below that the conical intersection (CI) [3–8], whose geometrical structure is fragments-like, plays a crucial role in the unimolecular photochemistry of hydantoin.

It is well established that most photochemical reactions begin from an excited potential surface and then cross over to a lower surface along the reaction route. They subsequently arrive on the ground state surface through a series of radiationless transitions (i.e., CIs). Eventually, they generate the photoproducts on the ground state surface [3–8]. That is to say, it is the presence of minima and transition states on the ground and excited state that controls the photochemical reactions [3–8].

2. Methodology

The theoretical results of the *ab initio* complete active space multiconfiguration self-consistent field (CASSCF) level of theory were achieved using the Gaussian 09 software package [9]. In this work, six σ, six π, and four nonbonding orbitals were selected as active orbitals. In addition, the optimization of CIs was achieved in the (*f*-2)-dimensional intersection space using the method of Robb et al. implemented in the Gaussian 09 program [9]. As a result, the 22 electrons in 16 orbitals CASSCF method was utilized with the 6-31G(d) basis sets (CAS(22,16)/6-31G(d)) for geometrical optimization.

The multireference Møller-Plesset (MP2-CAS) algorithm [10], which is given in the program package GAUSSIAN 09 [9], has also been utilized to compute dynamic electron correlations. In this work, the relative energies mentioned in the text are those determined at the MP2-CAS-(22,16)/6-311G(d) level using the CAS(22,16)/6-31G(d) (hereafter designed MP2-CAS and CASSCF, respectively) geometry.

3. Discussion

The central feature of the photochemical mechanism of **1** is the location of CI in the ground and excited electronic states. In this work, we shall use the molecular orbital (MO) model as presented in **Figure 1** as a basis for the interpretation of the phototransformation mechanism

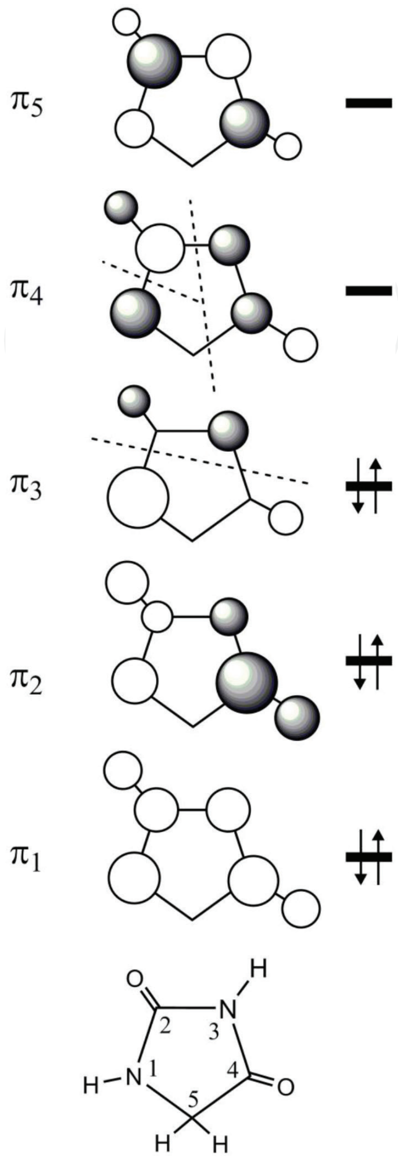


Figure 1. A π molecular orbital diagram for hydantoin (**1**).

of **1**. From **Figure 1**, one may see that two node planes (dashed lines) existing on the lowest molecular orbital (LUMO) are between N_1C_2, C_2N_3, and N_4C_5 atoms, whereas only one node plane exists on the highest molecular orbital (HOMO). These phenomena strongly imply the photofragmentation behaviors of hydantoin (**1**).

Figure 2 contains all the relative energies of the key points with respect to the energy of the reactant, **1**. Moreover, the geometrical structures of these points on the possible mechanistic pathway of **Figure 2** are demonstrated in the same figure.

At the beginning, **1** is promoted to its excited singlet state by a vertical excitation as shown in the left-hand side of **Figure 2**. Our MP2-CAS vertical excitation energy to the lowest excited S_1 state of **1** was computed to be 127 kcal/mol. However, according to the available experimental report

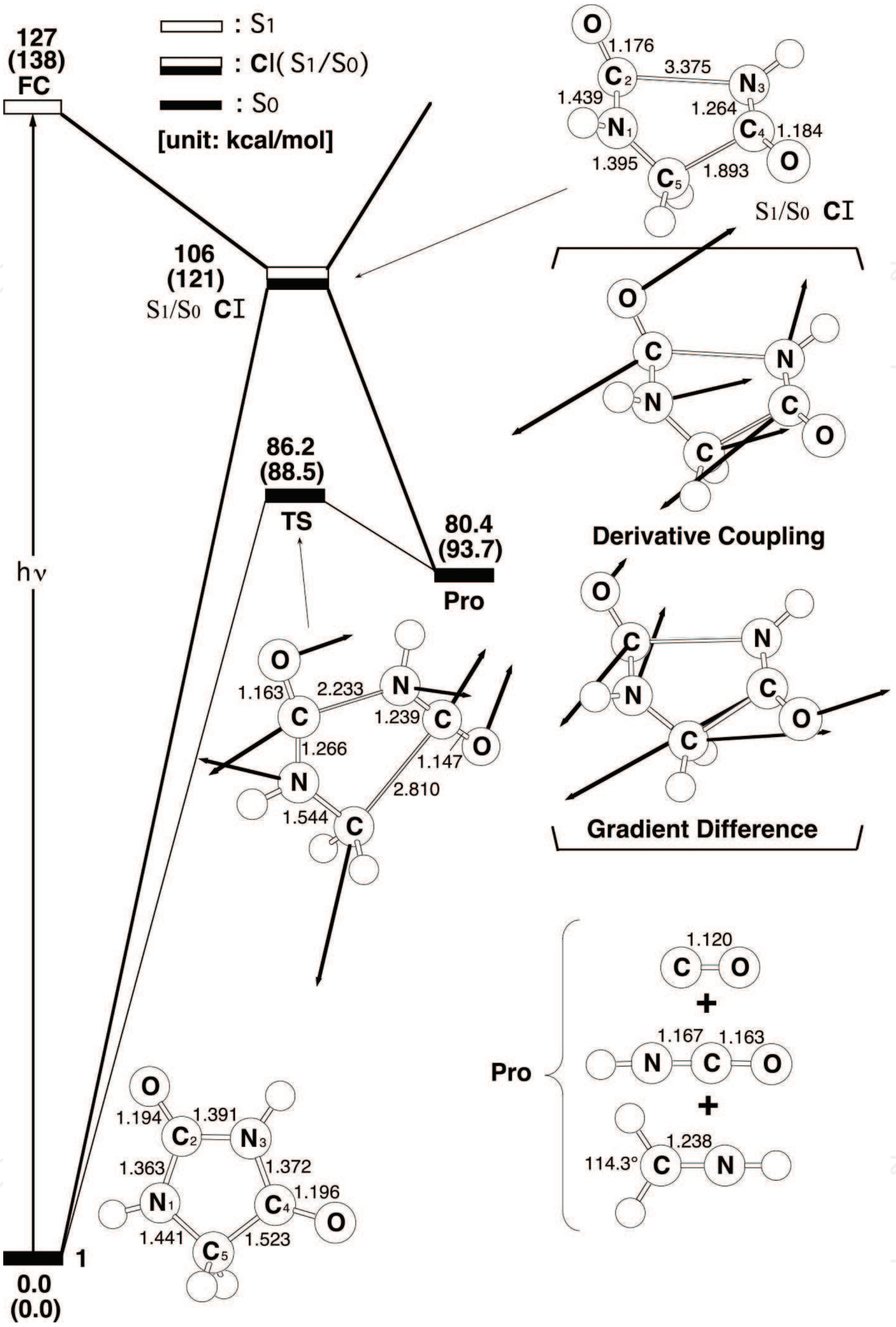


Figure 2. Potential energy surfaces for the fragmentation reaction of hydantoin (**1**). The abbreviations **FC**, **TS**, **CI**, and **Pro** stand for Franck-Condon, transition state, conical intersection, and products, respectively. The relative energies were obtained at the MP2-CAS-(22,16)/6-311G(d)//CAS(22,16)/6-31G(d) and CAS(22,16)/6-31G(d) (in parentheses) levels of theory. The selected geometrical parameters (Å) of CASSCF optimized structures of the stationary points are also given. Hydrogen is omitted for clarity. The heavy arrows in the **TS** indicate the main atomic motions in the transition state eigenvector. For more information, see the text.

shown in **Scheme 1**, the experimental wavelength $\lambda = 230$ nm (=124.3 kcal/mol in energy) [2] is somewhat lower than our computational data. Nevertheless, it is believed that the present calculations should provide a good estimate of the relative energies for the parent hydantoin (**1**) system.

As seen in **Figure 2**, after the vertical excitation process, **1** is located on the excited singlet surface but still possesses the S_0 (ground state) geometry (**FC**). From the point reached by the vertical excitation, **1** relaxes to reach an S_1/S_0 **CI**, where the photoexcited system decays nonradiatively to S_0. Examining the geometrical structure of **CI** given in **Figure 2**, it is noteworthy that its $N_1—C_2$, $C_2—N_3$, and $C_4—C_5$ bond distances were calculated to be 1.439, 3.375, and 1.893 Å, respectively, which strongly imply that these chemical bonds are easily broken due to the node planes appeared between these atoms in the LUMO, as already schematically illustrated in **Figure 1**. The computational results predicted that the energy of S_1/S_0 **CI** lies 106 kcal/mol above **1** and 21 kcal/mol below **FC** at the MP2-CAS level of theory. Funneling through S_1/S_0 **CI**, different reaction pathways on the ground state surface may be anticipated by following the derivative coupling vector or the gradient difference vector directions.[2] **Figure 2** shows that the derivative coupling vector is mainly related to the N_1C_2, C_2N_3, and C_4C_5 stretching modes that give three kinds of fragment products (i.e., CO, isocyanic acid, and methylenimine) on the S_0 surface. On the other hand, gradient difference vector gives the asymmetric $C_2N_1C_5C_4$ bending motion that may lead to a vibrationally hot **1**-S_0 species. It has to be noted that this photoreaction path is a one-step process (the direct mechanism), which only involves the S_1/S_0 **CI** point. Besides, this work predicts that the reaction pathway for the photofragmentation of **1** should be a barrierless route. In consequence, the process of the photochemical reaction path can be represented as follows (**Figure 2**):

$$\mathbf{1} \rightarrow \mathrm{FC} \rightarrow \mathbf{S_1/S_0}\,\mathrm{CI} \rightarrow \mathrm{CO} + \mathbf{H{-}N{=}C{=}O} + \mathbf{H{-}N{=}}\,\mathrm{CH_2}$$

This work also examined the thermal reaction (**Scheme 1**) on the ground state (S_0) potential energy surface using the same levels of theory. In spite of the fact that photoexcitation elevates **1** into an excited electronic state, it was already emphasized that the products of the photochemical reaction are influenced by the S_0 potential surface [2]. If one searches for transition states on the S_0 surface near the structure of S_1/S_0 **CI**, one may obtain **TS**. From **Figure 2**, the energy of the **TS** connecting **1** and **Pro** on the S_0 surface lies about 20 kcal/mol below that of the S_1/S_0 **CI**. It should be mentioned here that the calculated results reveal the energy barriers for **1** → **Pro** and **Pro** → **1** are estimated to be 86 and 6.0 kcal/mol, respectively. This theoretical evidence indicates that it would be difficult to generate the three fragments (i.e., CO, isocyanic acid, and methylenimine) under the thermal (dark) reaction, which agrees well with the experimental observations [2].

Besides these, one may argue that it is possible to have radical formation in such a photofragmentation reaction. In fact, the CAS(22,16)/6-31G(d) method has been used to calculate the energies of some radicals (such as HN=C=O• and CO•). Their relative energies, however, are higher than that of the **CI** (121 kcal/mol, at most 133 kcal/mol). Therefore, the radical mechanism is not considered in this work.

4. Conclusion

In conclusion, the present theoretical computations demonstrate that upon absorption of a photon of light, the hydantoin (**1**) is excited vertically to S_1 (FC) via a $^1(\pi \rightarrow \pi^*)$ transition.

Subsequently, the excited **1** can enter an extremely efficient channel. From the **CI** point, **1** continues its development on the ground state potential surface to yield the photoproduct through either the radiationless path or return to **1** at the singlet ground state. Additionally, the theoretical examinations suggest that no other radicals exist in such a photofragmentation reaction. Also, the theoretical findings indicate that under the thermal procedures, the fragmentation reaction of **1** should be failed. All these theoretical findings can give successful explanations for the available experimental finding [2].

Acknowledgements

The author is grateful to the National Center for High-Performance Computing of Taiwan for generous amounts of computing time, and the Ministry of Science and Technology of Taiwan for the financial support. The author also wishes to thank Professor Michael A. Robb, Dr. Michael J. Bearpark, Dr. S. Wilsey, (University of London, UK) and Professor Massimo Olivucci (Universita degli Studi di Siena, Italy) for their encouragement and support during his stay in London.

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