

The Study of Adsorption Structures of 3-Methyl-5-Pyrazolone on the Ge(100) Surface

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Received July 6, 2014, Accepted August 20, 2014

The most stable adsorption structures and energies of four tautomers of 3-methyl-5-pyrazolone (keto-1, enol-1, keto-2, and enol-2) on Ge(100) surfaces were investigated using density functional theory (DFT) calculations. The enol-1, keto-2, and enol-2 tautomers, but not the keto-1 tautomer, were found to exhibit stable adsorption structures on the Ge(100)-2 × 1 surface. Of these three adsorption structures, that of enol-2 is the most stable.

Key Words : Tautomerism, 3-Methyl-5-pyrazolone, Density functional theory (DFT) Calculation, Ge(100) surface

Introduction

Since density function theory (DFT) calculations were developed by Hohenberg and Kohn in 1964, this method has been used to simulate experimental data and molecular dynamics.¹ The good correspondence between DFT results and experimental data have led to DFT playing a pivotal role in the prediction of the behaviors of molecules.² Our group has for several years studied the properties of the molecular adsorption structures of biologically important organic molecules, such as amino acids, on the Ge(100) surface using DFT calculations in an effort to characterize their selectivities and stabilities.³⁻⁷

We selected the Ge(100) surface for these studies because of its zwitterionic properties, which mean that it can function as a Lewis acid or a Lewis base in the presence of biomolecules and organic molecules through diverse types of adsorption such as σ bond dissociation or dative bond formation.⁸⁻¹²

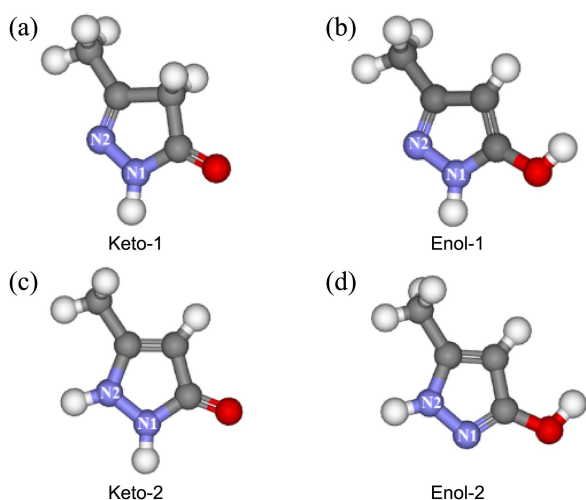
Although there have been numerous studies of the adsorption of pyrazolone derivatives,^{13,14} to date no study has examined the adsorption of 3-methyl-5-pyrazolone onto the Ge(100) surface. It is well-known that pyrazolone derivatives such as dipyrone, 1-phenyl-3-methyl-5-pyrazolone, and antipyrine can be used as analgesics.¹⁵ Therefore, knowledge of the adsorption behavior of pyrazolone derivatives could potentially be valuable for pharmaceutical applications.

There are several possible binding sites for 3-methyl-5-pyrazolone on the Ge(100) surface because the molecule contains two nitrogen atoms (a nitrogen next to an oxygen, N1, and a nitrogen far from an oxygen, N2) and one oxygen atom in its heterocyclic ring. Moreover, it has four tautomeric forms (keto-1, enol-1, keto-2, and enol-2; see Scheme 1). In the keto form, the oxygen atom is dative-bonded, whereas in the enol form the oxygen atom and one nitrogen atom are not protonated. In other words, the tautomerization of 3-methyl-5-pyrazolone has significant effects on its chemical reactivity that result in various adsorption structures on Ge(100) surfaces. Many researchers have studied these tautomers in aqueous solution, particularly the responses of the structures to changes in pH.^{16,17}

Here, we focused on determining the adsorption selectivities of the four tautomers of 3-methyl-5-pyrazolone on the Ge(100) surface and the stabilities of the adsorbed tautomers. We determined the stable adsorption structures and geometric configurations theoretically, and found which adsorption structure is the most stable at room temperature, by performing DFT calculations.

Experimental

DFT calculations were conducted to predict the energetics of the reaction pathways and the geometrically optimized structures of the 3-methyl-5-pyrazolone tautomers adsorbed on the Ge(100) surface. All DFT adsorption energy calculations were carried out using a hybrid density functional method implemented with the JAGUAR 9.1 software package that included Becke's three-parameter nonlocal exchange



Scheme 1. The four tautomers of 3-methyl-5-pyrazolone: (a) keto-1, (b) enol-1, (c) keto-2, and (d) enol-2. The gray, blue, red, and white balls correspond to carbon (C), nitrogen (N), oxygen (O), and hydrogen (H) atoms, respectively.

functional with the correlation functional of Lee–Yang–Parr (B3LYP). These calculations considered models consisting of four dimer clusters ($\text{Ge}_{35}\text{H}_{32}$). The geometries corresponding to the important local minima on the potential energy surface were determined at the B3LYP/LACVP** level of theory.^{18–20} The LACVP** basis set is a mixed basis set that uses the LACVP basis set to describe Ge atoms and the 6-31G basis set to describe the remaining atoms. The LACVP basis set describes atoms beyond Ar in the periodic table by using the Los Alamos effective core potentials developed by Hay and Wadt.^{21,22} For each cluster, optimization was performed by fixing the bottom two layers of Ge atoms in ideal Ge crystal positions while allowing the top layer of Ge atoms (including the dimer atoms) and the atoms of the chemisorbed adsorbate to relax. The geometries of the important local minima and the transition states on each energy surface were calculated. The optimizations of the local minima and transition states were performed with the same basis sets.^{23–26}

Results and Discussion

First, we calculated the adsorption structures of keto-1 on the Ge(100) surface, as shown in Figure 1. The keto-1 tautomer could in principle absorb on the Ge(100) surface at room temperature in either an O dative-bonded structure or a N2 dative-bonded structure. Because of absence of any hydrogen which can make a “H dissociation bonded structure” on an oxygen and a nitrogen 2 in keto-1, only an O dative-bonded structure and a N2 dative-bonded structure are available. The O dative and the N dative-bonded structure have -32.39 kcal/mol and -8.41 kcal/mol of adsorption energies by DFT calculations. These results confirm that keto-1 is more likely to absorb on the Ge(100) surface in the O dative-bonded structure, although the DFT calculations do suggest that a N dative-bonded structure is also possible.

Second, we calculated the stable adsorption energies of

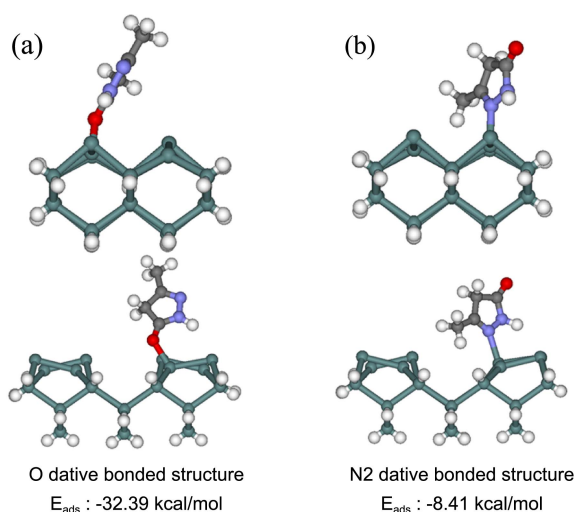


Figure 1. Possible adsorption structures and adsorption energies of keto-1 on the Ge(100) surface: (a) the O dative-bonded structure, and (b) the N2 dative-bonded structure.

enol-1 (see Scheme 1(b)). As shown in Figure 2, there are two reaction pathways to stable adsorption structures for enol-1 on the Ge(100) surface. One reaction pathway (top panel) is that from the O dative-bonded structure to the O-H dissociated N2 dative-bonded structure, which passes through two transition states, and the other reaction pathway (bottom panel) is that from the N2 dative-bonded structure to the N2 dative O-H dissociated bonded structure, which passes through one transition state. A reaction pathway was considered to be plausible if the final state has a more stable structure and the transition state energy is negative. The reaction pathways in Figure 2 were examined according to these criteria. The energy of the first transition state in the top panel is positive ($+4.08$ kcal/mol), which means that this reaction pathway is not plausible at room temperature on the Ge(100) surface. In contrast, the energy of the transition state of the reaction pathway in the bottom panel of Figure 2 is negative (-14.343 kcal/mol). Thus the bottom reaction

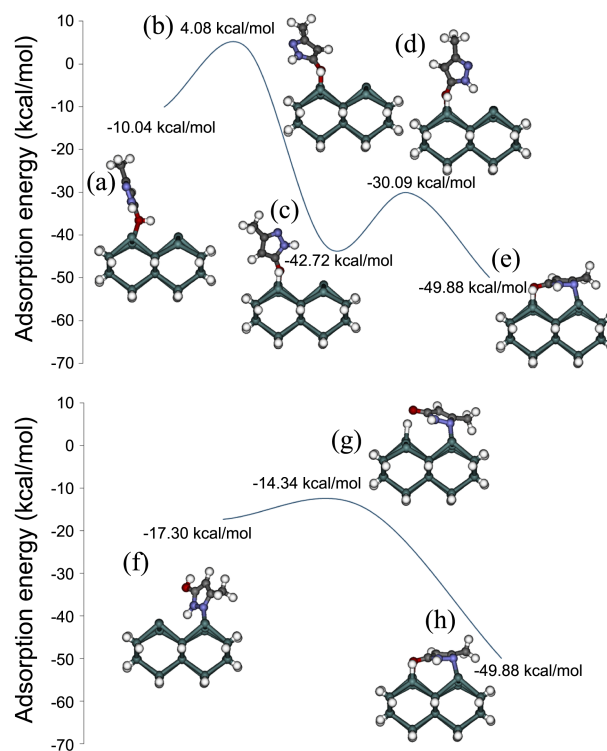


Figure 2. (Top) Calculated reaction pathway from the O dative-bonded structure to the O-H dissociated N2 dative-bonded structure, passing through two transition states, for enol-1 adsorbed on the Ge(100) surface: (a) the O dative-bonded structure, (b) the transition state between the O dative-bonded structure and the O-H dissociated bonded structure, (c) the O-H dissociated bonded structure, (d) the transition state between the O-H dissociated bonded structure and the O-H dissociated N2 dative-bonded structure, and (e) the O-H dissociated N2 dative-bonded structure. (Bottom) Calculated reaction pathway from the N2 dative-bonded structure to the N2-H dissociated O dative-bonded structure, passing through one transition states, for enol-1 adsorbed on the Ge(100) surface: (f) the N2 dative-bonded structure, (g) the transition state between the N2 dative-bonded structure and the N2 dative O-H dissociated bonded structure, and (h) the N2 dative O-H dissociated bonded structure.

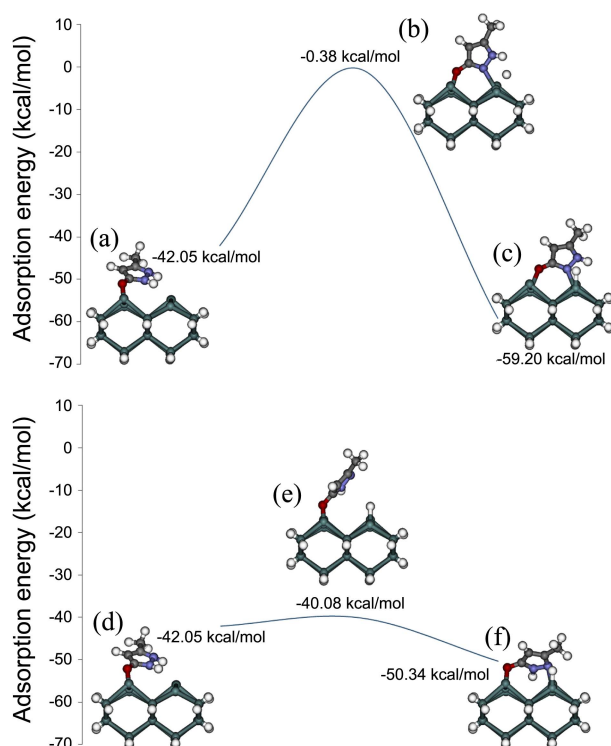


Figure 3. (Top) Calculated reaction pathway from the O dative-bonded structure to the O dative N1-H dissociation bonded structure, which passes through one transition states, for keto-2 adsorbed on the Ge(100) surface: (a) the O dative-bonded structure, (b) the transition state between the O dative-bonded structure and the O dative N1-H dissociated bonded structure, and (c) the O dative N1-H dissociated bonded structure. (Bottom) Calculated reaction pathway from the O dative-bonded structure to the O dative N2-H dissociated bonded structure, which passes through one transition states, for keto-2 adsorbed on the Ge(100) surface: (d) the O dative-bonded structure, (e) the transition state between the O dative-bonded structure and the O dative N2-H dissociated bonded structure, and (f) the O dative N2-H dissociated bonded structure.

pathway, which produces a stable enol-1 adsorption structure on the Ge(100) surface, is more plausible than the top reaction pathway.

Third, we performed DFT calculations to determine the stable adsorption structure and selectivity of keto-2 (see Scheme 1(c)) on the Ge(100) surface, as shown in Figure 3. As for enol-1, there are two possible adsorption structures for keto-2 on the Ge(100) surface: the O dative N1-H dissociation bonded structure (top panel) and the O dative N2-H dissociation bonded structure (bottom panel). Although the O dative N1-H dissociation bonded structure (top panel: -59.20 kcal/mol) is slightly more stable than the O dative N2-H dissociation bonded structure (bottom panel: -50.34 kcal/mol), the activation barrier of this pathway is higher than that leading to the O dative N2-H dissociation bonded structure. Therefore, the pathway starting from the O dative N2-H dissociation bonded structure is more stable for keto-2.

Finally, we calculated the adsorption structure of enol-2 (see Scheme 1(d)). As above, we considered a pathway that passes through two transition states to obtain a plausible

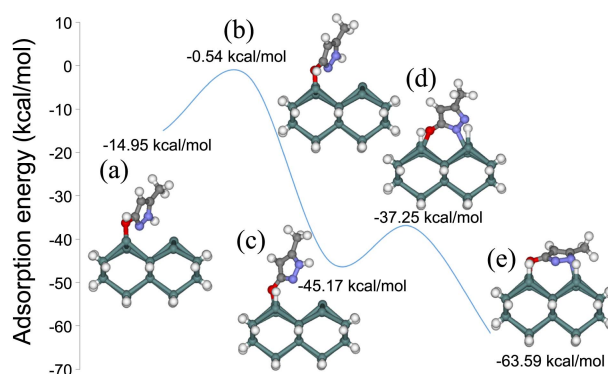


Figure 4. Calculated reaction pathway from the O dative-bonded structure to the O-H dissociated N2-H dissociation bonded structure, which passes through two transition states, for enol-2 adsorbed on the Ge(100) surface: (a) the O dative-bonded structure, (b) the transition state between the O dative-bonded structure and the O-H dissociated bonded structure, (c) the O-H dissociated bonded structure, (d) the transition state between the O-H dissociated bonded structure and the O-H dissociated N2 dative-bonded structure, and (e) the O-H dissociated N2-H dissociation bonded structure.

stable adsorption O-H dissociated N2-H dissociation bonded structure, as shown in Figure 4. One possible reaction pathway for enol-2 proceeds from the O dative-bonded structure to the O-H dissociated N2-H dissociation bonded structure. The structures in (a), (c), and (e) in Figure 4 have stable energy values and the energies of the two transition states ((b) and (d) in Figure 4) are both below zero, which means that this pathway is plausible.

Figure 5 shows the calculated bonding geometries of the enol-1, keto-2, and enol-2 tautomers on the Ge(100) surface. The tautomers all have stable absorption structures on the Ge(100) surface with the exception of keto-1: (a) the N2 dative O-H dissociation bonded structure, (b) the O dative N2-H dissociation bonded structure, and (c) the O-H dissociated N2-H dissociation bonded structure. These three adsorption structures all have negative energies and relatively small energy barriers, thus, they are stable. Of the three structures, the O-H dissociation N2-H dissociation bonded

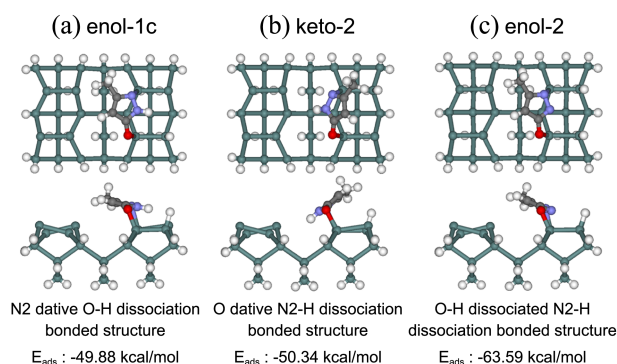


Figure 5. The most plausible structures of 3-methyl-5-pyrazolone on the Ge(100) surface: (a) enol-1 (N2 dative O-H dissociation bonded structure), (b) keto-2 (O dative N2-H dissociation bonded structure), and (c) enol-2 (O-H dissociated N2-H dissociation bonded structure).

structure of enol-2 has the lowest energy and is thus the most stable adsorption structure.

Conclusion

We have investigated the stable adsorption structures and energies of four tautomers (keto-1, enol-1, keto-2, and enol-2) of 3-methyl-5-pyrazolone on Ge(100) surfaces by performing DFT calculations. The enol-1, keto-2, and enol-2 tautomers, but not the keto-1 tautomer, have stable adsorption structures on the Ge(100)-2 × 1 surface according to our results for the activation barriers, transition state energies, and reaction pathways. Moreover, of the three possible adsorption structures, that of the enol-2 form, the O-H dissociated N2-H dissociation bonding structure, is the most stable.

Acknowledgments. This study was supported by a Sookmyung Women's University Research Grant 2014 (1-1403-0165).

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