**Ab Initio Study on the Interaction of CO₂ to the Acetate**

Namseok Kim, Soon Kwan Jeong,† Sungho Yoon,* and Gyoosoon Park‡

Department of Bio & Nano Chemistry, College of Natural Sciences, Kookmin University, Seoul 136-702, Korea
*E-mail: yoona@kookmin.ac.kr (Sungho Yoon); gpark@kookmin.ac.kr (Gyoosoon Park)

†Greenhouse Gas Research Center, Korea Institute of Energy Research, Daejeon 305-343, Korea

Received September 14, 2011, Accepted October 12, 2011

**Key Words :** Absorbent, CO₂, Carboxylate, Ab initio

The increasing CO₂ concentration in the atmosphere, which has been attributed to the burning of fossil fuels, is considered a major reason for global warming and a great threat to the environment. Because plant exhaust emissions are one of the major sources of atmospheric CO₂, the separation and collection of CO₂ from the combustion of fossil fuel has attracted worldwide attention. Therefore, it is important to examine techniques for the capture and release of CO₂.

Lewis bases, such as water, amines and amides, have been used as CO₂ absorbents because CO₂ acts as a Lewis acid. A group of carboxylate anions is one type of popular Lewis bases. Recently, the possibility of amino acids with a group of carboxylate anions is one type of popular Lewis bases. Nevertheless, the interaction between the carboxylate anion and CO₂ has not been studied systematically. This study examined the interaction mode of CO₂ to carboxylate functionality (CO₂⁻) using ab initio calculations.† The acetate anion (MeCO₂⁻) was chosen as a model in this study.

This study was initiated by performing HF/6-31+G(d) calculations for [MeCO₂CO₂⁻] complex, where the CO₂ molecule is located in the middle of the oxygen atoms of the carboxylate anion. The optimized geometry obtained by the HF/6-31+G* method remains relatively constant with the re-optimized geometry obtained using the MP2/6-31+G* method. The B3LYP/6-31+G* optimized structure and geometry, however, differs from the MP2/6-31+G* structure. m1 and b1, shown in Figure 1, are the optimized structure of the [MeCO₂-CO₂⁻] complex obtained by MP2/6-31+G* and B3LYP/6-31+G*, respectively. In the minimum energy structure, m1, the CO₂ molecule is perpendicular to plane of O2-C1-O3 and the C1' atom of CO₂ is positioned at the center between O2 and O3 of carboxylate. The angle $\theta_1$ (C1'-O2-C1) in m1 is 90.28°. In b1, however, the position of the C1' atom of CO₂ is predicted to be near one side. The angle $\theta_1$ (C1'-O2-C1) was 117.50°

To determine the other energy minima, the energy profile of the [MeCO₂-CO₂⁻] complex was examined by changing the relative position of CO₂ to a carboxylate anion. The analysis was carried out using MP2/6-31+G* and B3LYP/6-31+G* methods by varying the angle $\theta_1$ (C1'-O2-C1) from 50° to 260° by 10°. This result is shown in Figure 2. The other energy minimum structure was found to be at an angle(θ) of 238.13° for b2 and 232.40° for m2 using B3LYP/6-31G* and MP2/6-31G* methods, respectively. The geometries and binding energies of the complexes (m1, b1, m2, and b2) are listed in Table 1.

**Table 1.** The representative geometrical parameters and binding energies for the [MeCO₂-CO₂⁻] complexes

<table>
<thead>
<tr>
<th>Method</th>
<th>$\theta_1$, $\theta_2$</th>
<th>$\phi_1$, $\phi_2$</th>
<th>$d_1$</th>
<th>$d_2$</th>
<th>$d_3$</th>
<th>BE, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP2</td>
<td>m1</td>
<td>90.28</td>
<td>168.98</td>
<td>-92.80</td>
<td>92.14</td>
<td>2.667</td>
</tr>
<tr>
<td></td>
<td>m2</td>
<td>232.40</td>
<td>169.58</td>
<td>-13.33</td>
<td>167.00</td>
<td>2.471</td>
</tr>
<tr>
<td>B3LYP</td>
<td>b1</td>
<td>117.50</td>
<td>145.96</td>
<td>-91.83</td>
<td>91.90</td>
<td>1.804</td>
</tr>
<tr>
<td></td>
<td>b2</td>
<td>238.13</td>
<td>139.08</td>
<td>-64.28</td>
<td>117.93</td>
<td>1.620</td>
</tr>
</tbody>
</table>

*: $\angle$ (C1'-O2-C1', degree), $\theta_1$ (O2-C1'-O3', degree), $\phi_1$ (C1'-O2-C1'-O3', degree), $\phi_2$ (C1-O2-C1'-O3', degree), $\theta_1$ (O2-C1', Å), $\theta_2$ (C1'-O2', Å), $\theta_3$ (C1'-O3', Å), BE, binding energy (kcal/mol), $b^{TS}$, saddle point between two minima of b1 and b1

**Figure 1.** Optimized structures of [MeCO₂-CO₂⁻] complexes obtained by B3LYP/6-31G* (b1 & b2) and MP2/6-31G* (m1 & m2).
The analysis of charge distribution for the \[\text{MeCO}_2\text{CO}_2^−\] complexes \(^a\) and \(^b\).

<table>
<thead>
<tr>
<th>Method</th>
<th>(zC1)</th>
<th>(zO2)</th>
<th>(zO3)</th>
<th>(zC1')</th>
<th>(zO2')</th>
<th>(zO3')</th>
<th>(Z_{\text{CO2}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP2</td>
<td>(0.707/0.428)</td>
<td>(-0.776/−0.651)</td>
<td>(-0.776/−0.651)</td>
<td>(0.920/0.672)</td>
<td>(-0.460/−0.336)</td>
<td>(-0.460/−0.336)</td>
<td>(0.000/0.000)</td>
</tr>
<tr>
<td>(\text{MeCO}_2\text{CO}_2^−)</td>
<td>(0.834/1.100)</td>
<td>(-0.765/−0.817)</td>
<td>(-0.764/−0.817)</td>
<td>(0.929/0.841)</td>
<td>(-0.478/−0.472)</td>
<td>(-0.479/−0.474)</td>
<td>(-0.028/−0.105)</td>
</tr>
<tr>
<td>(m1)</td>
<td>(0.732/0.535)</td>
<td>(-0.802/−0.679)</td>
<td>(-0.749/−0.626)</td>
<td>(0.920/0.688)</td>
<td>(-0.486/−0.376)</td>
<td>(-0.474/−0.359)</td>
<td>(-0.040/−0.047)</td>
</tr>
</tbody>
</table>

\(^a\)Calculated using MP2/6-31+G\(^*\) and B3LYP/6-31+G\(^*\). \(^b\)The values is indicated for (Mulliken charge)/(CHelpG charge). \(^c\)Total charge of \(\text{CO}_2\).
of the O atoms of the acetate anion, which corresponds to mode B (θ ~110°). Another minimum was located between the range of (θ = -230-250°), which corresponds to mode C. The two minimum positions for each calculation were found, as shown in Figure 4(a) and 4(b). One common position (mode C, b2 & m2) was found as the global/local minimum site for binding between the CO2 molecule and acetate anion. The bridging structure of m1 (mode A) was observed in the HF and MP2 calculation. On the other hand, b1 (mode B) was predicted as another binding mode in the B3LYP method. Although these methods tested did not predict the same interactions, they clearly indicate three possible interaction sites between CO2 (Lewis acid) and acetate anion (Lewis base). The interaction of carboxylate anions and metal cations, which is another representative Lewis acid, has been an interesting topic in inorganic and biological chemistry. Three classic bond modes are proposed based on the reported crystal structures of coordinated carboxylate metal complexes, as depicted in Figure 4(c). The theoretical predictions of the three interaction modes of A–C were well-matched with the reported coordinated crystal structures for carboxylate-metal complexes of M1–M5.6

To confirm the possibility of carboxylate anions as the absorbent for CO2, the binding energy between them was calculated as the energy difference between the optimized energies of the {CO2 + carboxylate anion} complex and the optimized energies of the separate CO2 plus carboxylate anion. For all types of interaction modes of CO2 to the acetate anion complex, the predicted binding energies ranged from 8.6 to 11.01 kcal/mol in both methods. The BE for bTS was 9.35 kcal/mol, which is almost 3 times larger than the interaction between MEA and CO2 molecule (3.57 kcal/mol).3 This highlights the possibility of the carboxylate anion as a new efficient group in the absorbents for the CO2 molecule.

In summary, this study evaluated the possibility of amino acids with a carboxylate motif as potential absorbents of CO2 molecules in Carbon Capture and Sequestration (CCS). The stable structures of mono CO2 complexes with an acetate anion were determined using ab initio methods HF, B3LYP, and MP2 using a 6-31+G(d) basis set. Based on the results, there were 3 possible interaction modes between the CO2 molecule and acetate anion. The higher binding energy (ca. 9 kcal/mol) resulted in an interaction between the CO2 molecule and acetate anion, compared to that (ca. 3.5 kcal/mol) for the interaction between MEA and CO2. This suggests that the carboxylate anion is a potential candidate to replace the current absorbent, MEA, in CO2 separation. Although the 1:1 interaction between CO2 and acetate anion were handled in this report, the possibility and binding energies of a 1:2 interaction between them should also be addressed in the near future.

Computational Method. Calculations of the molecules were performed using the GAUSSIAN 03 program.5 Geometry optimizations were carried out without restricting any symmetry at the B3LYP(DFT) and MP2 level using the 6-31+G* basis set.6 Harmonic vibrational frequencies calculated at the same level were used to characterize the stationary points. The number of imaginary frequencies (0 or 1) indicates whether a minimum or a transition state has been located. The transition structure of bTS in B3LYP/6-31+G* was obtained from a TS optimization, and was confirmed with the normal mode corresponding to the imaginary frequency.

Acknowledgments. We acknowledge the financial support by grants from Korea CCS R&D Center, funded by the Ministry of Education, Science and Technology of Korean government, and the Research Program 2011 of Kookmin University.

References