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Ab Initio Study on the Interaction of CO_2 to the Acetate

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The increasing CO_2 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 CO_2, the separation and collection of CO_2 from the combustion of fossil fuel has attracted worldwide attention. Therefore, it is important to examine techniques for the capture and release of CO_2.

Lewis bases, such as water, amines and amides, have been used as CO_2 absorbents because CO_2 acts as a Lewis acid. A group of carboxylate anions is one type of popular Lewis base. Recently, the possibility of amino acids with a carboxylate motif as a potential absorbent of CO_2 was identified in an experimental study.[1] The carbonyl group in acetone can weakly interact with CO_2 with a binding energy of 3-5.2 kcal/mol,[2] which again suggests the possibility of the carboxylate anion as an electron donor. A stronger interaction between carboxyl groups and CO_2 compared to carbonyl compounds is expected because the anion charge is delocalized over two O donors in the carboxylate anion. Nevertheless, the interaction between the carboxylate anion and CO_2 has not been studied systematically. This study examined the interaction mode of CO_2 to carboxylate functionality (CO_2^-) using *ab initio* calculations.[3] The acetate anion ($MeCO_2^-$) was chosen as a model in this study.

This study was initiated by performing HF/6-31+G(d) calculations for $[MeCO_2 \cdot CO_2]^-$ complex, where the CO_2 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 $[MeCO_2 \cdot CO_2]^-$ complex obtained by MP2/6-31+G* and B3LYP/6-31+G*, respectively. In the minimum energy structure, **m1**, the CO_2 molecule is perpendicular to plane of O2-C1-O3 and the C1' atom of CO_2 is positioned at the center between O2 and O3 of carboxylate. The angle θ_1 (C1'-O2-C1) in **m1** is 90.28°. In **b1**, however, the position of the C1' atom of CO_2 is predicted to be near one side. The angle θ_1 (C1'-O2-C1) was 117.50°.

To determine the other energy minima, the energy profile of the $[MeCO_2 \cdot CO_2]^-$ complex was examined by changing the relative position of CO_2 to a carboxylate anion. The analysis was carried out using MP2/6-31+G* and B3LYP/6-31+G* methods by varying the angle θ_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 MP2/6-31+G* methods, respectively. The geo-

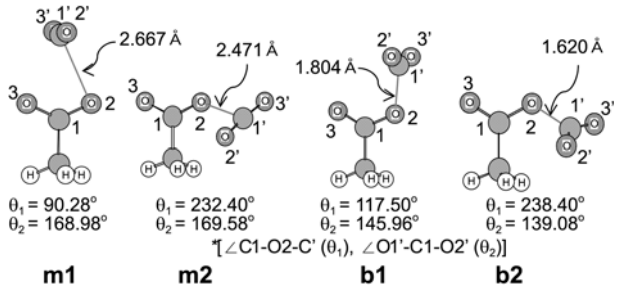

Figure 1. Optimized structures of $[MeCO_2 \cdot CO_2]^-$ complex obtained by B3LYP/6-31G* (**b1** & **b2**) and MP2/6-31+G* (**m1** & **m2**).

Table 1. The representative geometrical parameters and binding energies for the $[MeCO_2 \cdot CO_2]^-$ complexes

Method		θ_1[a]	θ_2[b]	ϕ_1[c]	ϕ_2[d]	d_1[e]	d_2[f]	d_3[g]	BE[h]
MP2	**m1**	90.28	168.98	-92.80	92.14	2.667	1.184	1.184	11.014
	m2	232.40	169.58	-13.33	167.00	2.471	1.184	1.183	8.633
B3LYP	**b1**	117.50	145.96	-91.83	91.90	1.804	1.206	1.206	9.888
	b2	238.13	139.08	-64.28	117.93	1.620	1.225	1.221	10.360
	$\mathbf{b}^{TS}$[i]	91.18	166.96	-92.48	93.11	2.649	1.175	1.175	9.347

[a]θ_1 (∠C1-O2-C1', degree). [b]θ_2 (∠O2'-C1'-O3', degree). [c]ϕ_1 (∠C1-O2-C1'-O2', degree). [d]ϕ_2 (∠C1-O2-C1'-O3', degree). [e]δ_1 (O2-C1', Å). [f]δ_2 (C1'-O2', Å). [g]δ_3 (C1'-O3', Å). [h]BE, binding energy (kcal/mol). [i]$\mathbf{b}^{TS}$, saddle point between two minima of **b1** and **b1'**

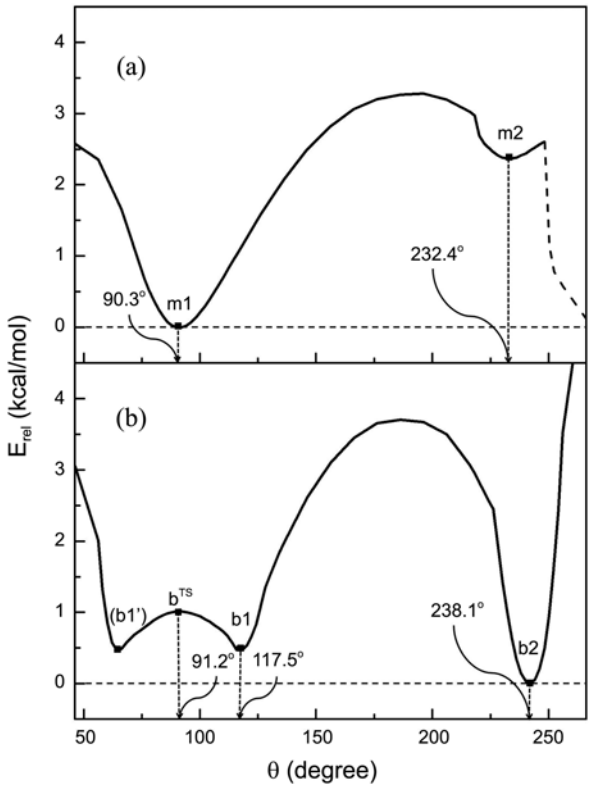

Figure 2. Potential energy curves of the [$MeCO_2 \cdot CO_2$] complex due to varying the angle (C1'-O2-C1, degree). (a) MP2/6-31+G*, (b) B3LYP/6-31+G*.

metry of b1' is an identical mirror image of b1 with same energy. The geometries of **b2** and **m2** are similar to each other (see Figure 1). Table 1 summarizes the representative parameters for **m1**, **b1**, **m2**, and **b2**.

As shown in Table 1, structure of the global minimum differs according to the optimization methods. According to the MP2/6-31+G* method, the relative energy of **m1** was predicted to be 2.38 kcal/mol lower than **m2**. The binding energy of the global minima **m1** was predicted to be 11.01 kcal/mol. In the case of B3LYP/6-31+G* optimization, the binding energy of **b2** was predicted to be 10.36 kcal/mol. The **b2** structure is the global minimum and is energetically 0.47 kcal/mol more stable than **b1**. The distance of the $C_{CO2} \cdots O_{acetate}$ interaction in **b1**, 1.804 Å, is nearly 0.863 Å

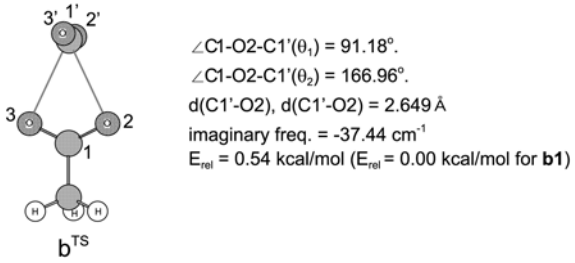

Figure 3. Transition state structure of $\mathbf{b}^{TS}$ optimized using B3LYP/6-31+G*.

shorter than that in **m1**, because the bridging **m1** site often locates much closer than mono binding **b1** site. Distance for another mono binding site (**b2**), 1.620 Å, has very close with the one of **b1** site. In the DFT study, the saddle point $\mathbf{b}^{TS}$, whose structure shows similar geometry to **m1**, might be located between two minima of **b1** and **b1'**, as shown in Figure 2. The energy for saddle point $\mathbf{b}^{TS}$, was predicted to be slightly higher than **b1**. The difference in energy between **b1** (or **b1'**) and $\mathbf{b}^{TS}$ was predicted to be 0.54 kcal/mol (see Figure 3).

The CO_2 molecule is bent slightly when it interacts with the carboxylate anion, indicating the transfer of electron density to the carbon atom of CO_2. Table 2 lists the results of charge distributions analysis (Mulliken and CHelpG charges). In the $MeCO_2^-$ ion, the negative charge is delocalized on two oxygen atoms (O2 and O3). The electron density moves from the Me CO_2^- ion to the CO_2 molecule in the $CO_2 \cdot$Me CO_2^- complex. It shows an increase in the total charge at CO_2 (Z_{CO2}). For example, the CHelpG charges on **m1** and **b1** changed from zero to −0.105 and −0.331, respectively. Similar trends were observed in the Mulliken charge on their complexes. This shows that the acetate anion acts as a Lewis base during an interaction with CO_2.

Regarding the binding pattern of CO_2, it should be noted that there are 3 binding modes of **A**, **B** and **C**, as shown in Figure 4. In the cases of HF and MP2 optimization, the global minimum was observed when the CO_2 molecule is located in the middle of the oxygen atoms of the carboxylate anion, which corresponds to *mode A* (θ ~90°). On the other hand, in the case of the B3LYP study, the energy minimum was achieved when the CO_2 molecule exists on the top right

Table 2. The analysis of charge distribution for the [$MeCO_2 \cdot CO_2$]$^-$ complexes[a,b]

Method		zC1	zO2	zO3	zC1'	zO2'	zO3'	Z_{CO2}[c]
MP2	**CO_2**	–	–	–	0.920/0.672	−0.460/−0.336	−0.460/−0.336	0.000/0.000
	$MeCO_2^-$	0.707/0.428	−0.776/−0.651	−0.776/−0.651	–	–	–	–
	m1	0.834/1.000	−0.765/−0.817	−0.764/−0.817	0.929/0.841	−0.478/−0.472	−0.479/−0.474	−0.028/−0.105
	m2	0.732/0.535	−0.802/−0.679	−0.749/−0.626	0.920/0.688	−0.486/−0.376	−0.474/−0.359	−0.040/−0.047
B3LYP	**CO_2**	–	–	–	0.748/0.746	−0.374/−0.373	−0.374/−0.373	0.000/0.000
	$MeCO_2^-$	0.521/0.435	−0.641/−0.639	−0.641/−0.639	–	–	–	–
	b1	0.684/0.978	−0.449/−0.694	−0.588/−0.751	0.681/1.025	−0.526/−0.678	−0.526/−0.678	−0.371/−0.331
	b2	0.583/0.919	−0.400/−0.401	−0.552/−0.553	0.609/0.606	−0.551/−0.578	−0.581/−0.550	−0.523/−0.522

[a]Calculated using by MP2/6-31+G* and B3LYP/6-31+G*. [b]The values is indicadicated for (Mullikan charge)/(ChelpG charge). [c]Total charge of CO_2.

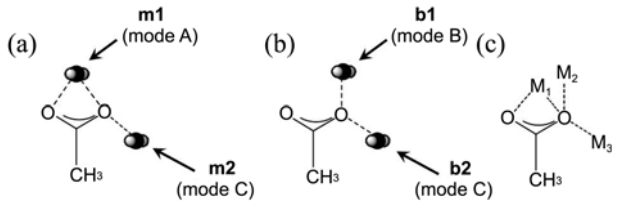

Figure 4. Possible directions of interaction of CO_2 on the acetic anion calculated from MP2 (a) and B3LYP (b). (c) Reported possible three sites of interaction between a metal cation (Lewis acid) and acetate anion (Lewis base).

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 CO_2 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 an 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 CO_2 (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 $\mathbf{M_1}$~$\mathbf{M_3}$.[4-6]

To confirm the possibility of carboxylate anions as the absorbent for CO_2, the binding energy between them was calculated as the energy difference between the optimized energies of the {CO_2 + carboxylate anion} complex and the optimized energies of the separate CO_2 plus carboxylate anion. For all types of interaction modes of CO_2 to the acetate anion complex, the predicted binding energies ranged from 8.6 to 11.01 kcal/mol in both methods. The BE for $\mathbf{b^{TS}}$ was 9.35 kcal/mol, which is almost 3 times larger than the interaction between MEA and CO_2 molecule (3.57 kcal/mol).[7] This highlights the possibility of the carboxylate anion as a new efficient group in the absorbents for the CO_2 molecule.

In summary, this study evaluated the possibility of amino acids with a carboxylate motif as potential absorbents of CO_2 molecules in Carbon Capture and Sequestration (CCS). The stable structures of mono CO_2 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 CO_2 molecule and acetate anion. The higher binding energy (*ca*. 9 kcal/mol) resulted in an interaction between the CO_2 molecule and acetate anion, compared to that (*ca*. 3.5 kcal/mol) for the interaction between MEA and CO_2. This suggests that the carboxylate anion is a potential candidate to replace the current absorbent, MEA, in CO_2 separation. Although the 1:1 interaction between CO_2 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.[8] Geometry optimizations were carried out without restricting any symmetry at the B3LYP(DFT) and MP2 level using the 6-31+G* basis set.[9] 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 $\mathbf{b^{TS}}$ in B3LYP/6-31+G* was obtained from a TS optimization, and was confirmed with the normal mode corresponding to the imaginary frequency.

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