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The effects of water microsolvation on the $C_2O_4^- \leftrightarrow CO_2{\cdot}CO_2^-$ core switching reaction: Perspective from exploration of pathways on the potential energy surfaces of small $[(CO_2)_2(H_2O)_n]^-$ ($n = 1$ and 2) clusters

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ABSTRACT

Water microsolvation effects on the $C_2O_4^- \leftrightarrow CO_2{\cdot}CO_2^-$ anion core switching reaction in the small $[(CO_2)_2(H_2O)_n]^-$ ($n = 1$ and 2) clusters have been computationally studied. All low-energy rearrangement pathways have been explored using global reaction route mapping (GRRM) techniques. Both the $C_2O_4^-$ dimer anion core and $CO_2{\cdot}CO_2^-$ monomer anion core have various hydration structures. The former is stable in $[(CO_2)_2(H_2O)_1]^-$ while the latter becomes stable in $[(CO_2)_2(H_2O)_2]^-$. It was found that the energy levels of the transition states significantly depend on the detailed hydration structures. We also performed Born-Oppenheimer molecular dynamics calculations to simulate photoelectron spectra of the $[(CO_2)_2(H_2O)_n]^-$ clusters.

1. Introduction

Size-selected clusters consisting of reactive molecules and solvent molecules have been extensively used to understand microsolvation effects on various chemical reactions at an atomic-level picture [1,2]. The $(CO_2)_2^-{\cdot}S_n$ anion cluster system (here S denotes a solvent molecule) has an interesting property due to the existence of the $C_2O_4^- \leftrightarrow CO_2{\cdot}CO_2^-/CO_2^-{\cdot}CO_2$ charge-transfer type reaction pathways [3–24]. Previous theoretical studies [23,24] have shown that the most stable isolated $C_2O_4^-$ anion has a symmetric D_{2d} structure, where an excess electron is equally distributed over the two equivalent bent OCO moieties in the D_{2d} form of $C_2O_4^-$. The potential energy surface of this anion system also has metastable local minima corresponding to the $CO_2^-{\cdot}CO_2$ anion-molecule complex (with C_s or C_{2v} symmetry), where the excess electron is mainly localized on the bent OCO moiety while the other nearly linear CO_2 molecule acts as a neutral solvent. Due to this unique charge-transfer nature, the $(CO_2)_2^-{\cdot}S_n$ cluster system frequently shows cluster size-induced core-switching behaviors, where the anion core in the cluster takes either the $C_2O_4^-$ (dimer core) or $CO_2^-{\cdot}CO_2$ (monomer core) form depending on the number of the solvent molecules. For example, Tsukuda et al. [7] have measured photoelectron spectra of $(CO_2)_2^-(CO_2)_n$ in the range of $0 \le n \le 14$ and found that n-dependence of the vertical detachment energy (VDE) shows sharp discontinuities between $n = 4$ and 5, and between $n = 11$ and 12. Since the dimer anion core generally has a larger VDE value than that of the monomer anion core, the nature of the anion core can be easily assigned from the peak VDE value of the measured photoelectron spectrum. They have concluded that the monomer anion core is preferentially formed in the clusters with the $n = 5$–11 range while the dimer anion core dominates for other clusters.

Photoelectron spectra of the hydrated $[(CO_2)_2(H_2O)_n]^-$ ($n = 0$–2) clusters have also been measured by Tsukuda et al. [8]. They concluded that hydration plays a more crucial role in the core-switching behavior even with smaller numbers of water molecules. More specifically, they have shown that both the monomer and dimer anion cores coexist in the $[(CO_2)_2(H_2O)_n]^-$ ($n = 1$ and 2), where the dimer anion core dominates for $n = 1$ while the monomer core dominates for $n = 2$. A similar experimental study has been carried out for the $(CO_2)_2^-(H_2O)_n$ ($n = 2$–11) clusters by Sanov and coworkers [15]. They have suggested the coexistence of both the dimer and monomer anion cores for $n = 2$ and 3. Interestingly, they have concluded that only the monomer anion core is preferentially formed in larger clusters of $n > 3$ although they did not completely exclude the coexistence of the dimer and monomer cores due to their experimental limitation. In addition to these photoelectron experiments, the core-switching phenomena in the

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$(CO_2)_2^-(H_2O)_n$ clusters have also been confirmed with an infrared absorption spectroscopy technique [14,17–19].

In this work we focus on the effects of H_2O microsolvation on the $C_2O_4^- \leftrightarrow CO_2{\cdot}CO_2^-$ charge-transfer reaction pathways using small hydrated clusters $[(CO_2)_2(H_2O)_n]^-$ ($n = 1$ and 2) from a theoretical viewpoint. There have been previous theoretical studies [17,22–25] on the $(CO_2)_2^-{\cdot}S_n$ clusters using *ab initio* electronic structure theory; however, most of previous studies focused on the stable geometric structures as well as their energetic stabilities and did not report reaction pathways between different local minimum structures nor transition state structures at all. Very recently, *ab initio* molecular dynamics simulations have been applied to the large $[(CO_2)_2(H_2O)_n]^-$ clusters and bulk solution system; however, core-switching was not observed unfortunately [26]. Therefore, it is quite interesting to understand the effects of H_2O microsolvation on the charge-transfer pathways although the actual calculations are limited to small clusters due to the complicated nature of the high-dimensionality potential energy surfaces of the $[(CO_2)_2(H_2O)_n]^-$ cluster system. In particular, it would be interesting to know how hydration motif changes transition state properties, their energetics and reaction coordinates since it is expected that polar water molecules can significantly affect the charge distributions in the anionic $C_2O_4^-$ moiety in the hydrated cluster depending on the hydrogen-bonding structure. We believe that such information would be useful for understanding of general charge transfer reaction mechanisms in condensed-phase polar solvents at a molecular level.

In order to understand the potential energy surface profiles of the $[(CO_2)_2(H_2O)_n]^-$ ($n = 1$ and 2) clusters, we here employ the GRRM (Global Reaction Route Mapping) computer code utilizing the powerful and automated scaled hypersphere search algorithm developed by Maeda and Ohno [27–30]. With this computational technique many low-lying structures as well as transition state structures on the potential energy surface can be automatically and systematically explored.

2. Computational details

All the GRRM calculations [27–30] have been done at the ωB97XD/aug-cc-pVDZ DFT level of theory using the Gaussian09 program [31]. The ωB97XD exchange-correlation functionals and the aug-cc-pVDZ basis set were chosen since the calculated VDE value of D_{2d}-$C_2O_4^-$ (3.44 eV) and the adiabatic electron affinity value of CO_2^- (-0.53 eV) reasonably reproduce the corresponding experimental values (3.0 [7] and -0.6 eV [32–34]). Table 1 presents the comparison of the adiabatic electron affinities and VDE values calculated with various DFT functionals. We have noticed that the larger aug-cc-pVTZ basis set gave somewhat better results (3.13 and -0.62 eV) but the GRRM calculations using this basis set were found to be too expensive. Since we are interested in energetically low-lying minimum structures as well as transition state structures on the potential energy surfaces, we have adopted the large-ADD (Anharmonic Downward Distortion) following method [30] implemented in the GRRM code [35] with *ladd*, *upDC* and *downDC* parameters being 5, 16 and 14, respectively.

In order to obtain more accurate relative energies, single point calculations were performed at the CCSD(T)/aug-cc-pVTZ level of theory for the $(CO_2)_2^-$ and $[(CO_2)_2(H_2O)_1]^-$ systems, although the CCSD(T)/aug-cc-pVDZ level has to be employed for the larger $[(CO_2)_2(H_2O)_2]^-$ cluster. The energetic accuracy of the CCSD(T) calculations for non-covalent interactions of neutral chemical systems has been frequently studied in the past [36,37]. However, its accuracy has not yet been fully established for the reaction pathways as well as transition states for the hydrated anionic systems containing charge-transfer processes. Therefore, in Table 2, we compare the relative energies for some structures on the reaction pathways for $C_2O_4^-$ and $[(CO_2)_2(H_2O)]^-$ (see Figs. 1 and 2). It is seen that the ωB97XD results are somewhat deviated from the CCSD(T) results while the differences in CCSD(T)/aug-cc-pVDZ energies and CCSD(T)/aug-cc-pVTZ energies are generally small.

Table 1

Comparison of adiabatic electron affinities (ΔE in eV) of the CO_2 monomer and vertical detachment energies (VDEs in eV) of the $C_2O_4^-$ dimer calculated using various DFT functionals.

DFT functional	$-\Delta E$	VDE
ωB97XD/6-31+G(*d*)	0.44	3.66
ωB97XD/6-311+G(*d*)	0.55	3.32
ωB97XD/aug-cc-pVDZ	0.53	3.44
ωB97XD/aug-cc-pVTZ	0.62	3.13
B3LYP/6-31+G(*d*)	0.27	3.60
B3LYP/6-311+G(*d*)	0.37	3.25
B3LYP/aug-cc-pVDZ	0.34	3.41
B3LYP/aug-cc-pVTZ	0.40	3.11
CAM-B3LYP/6-31+G(*d*)	0.26	3.75
CAM-B3LYP/6-311+G(*d*)	0.37	3.44
CAM-B3LYP/aug-cc-pVDZ	0.34	3.53
CAM-B3LYP/aug-cc-pVTZ	0.41	3.32
PBE/6-31+G(*d*)	0.34	0.52
PBE/6-311+G(*d*)	0.43	3.27
PBE/aug-cc-pVDZ	0.40	3.40
PBE/aug-cc-pVTZ	0.43	3.16
LC-ωPBE/6-31+G(*d*)	0.33	3.82
LC-ωPBE/6-311+G(*d*)	0.44	3.58
LC-ωPBE/aug-cc-pVDZ	0.42	3.66
LC-ωPBE/aug-cc-pVTZ	0.48	3.45
Experiment	0.6[a]	3.0[b]

[a] Taken from Refs. [32–34]. The adiabatic electron affinity is defined as the energy difference between the CO_2 and CO_2^- minima.

[b] Taken from Ref. [7].

We have also performed on-the-fly BOMD (Born-Oppenheimer Molecular Dynamics) calculations at the ωB97XD/aug-cc-pVDZ level to simulate experimentally measured photoelectron spectra of the $[(CO_2)_2(H_2O)_n]^-$ clusters. The BOMD method, which is implemented in the Gaussian09 programs, uses a fifth-order polynomial fitted to the energy, gradient, and Hessian at each time step, and then the step size is taken to be much larger than the step size used in the normal method employing only gradient information. From the results of harmonic vibrational analyses for selected clusters, the initial conditions for the trajectories were generated by allowing each normal vibrational mode to have its own zero-point energy. Trajectories were integrated for about 2 ps with a step size being 0.7–1.1 fs. The vertical detachment energy (VDE) values were then obtained for the neutral state with the geometry extracted at each step of the trajectory.

3. Results and discussion

Before presenting the computational results for the $[(CO_2)_2(H_2O)_n]^-$ clusters, we first discuss the potential energy surface of the bare $(CO_2)_2^-$ system. Saeki and coworkers [22–24] have previously studied the $C_2O_4^- \leftrightarrow CO_2{\cdot}CO_2^-$ reaction pathways and found three minimum structures (with D_{2d}, C_{2v}, and C_s structures) and two transition state structures for the $D_{2d} \leftrightarrow C_s$ and $C_{2v} \leftrightarrow C_s$ isomerization processes. The present GRRM calculations have given a total of eight minimum structures and eight transition state structures. The lowest three minimum structures were found to be essentially the same as the results of Saeki et al. [22–24]. Other high-lying five structures are not important from an energetic viewpoint. Fig. 1 schematically summarizes the low-lying reaction pathways on the $C_2O_4^-$ potential energy surface obtained from the GRRM calculations. The geometries of the two transition states for $D_{2d} \leftrightarrow C_s$ and for $C_s \leftrightarrow C_{2v}$ found in this work are very similar to the results