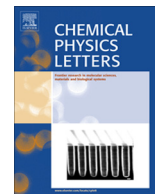




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Interactions of carbon dioxide with model organic molecules: A comparative theoretical study

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ABSTRACT

Interaction energies obtained using CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ computations including both ZPE and BSSE corrections range from -2.9 to -14.2 kJ mol⁻¹. While formic acid forms the most stable complex with CO₂, formaldehyde yields the least stable complex. Lewis acid–base interaction such as C–N···C(CO₂), C=O···C(CO₂), which overcomes C–H···O blue-shifting hydrogen bond, plays a significant role in stabilizing most complexes. However, the strength of (HCOOH, CO₂) is mainly determined by O–H···O red-shifting hydrogen bond. The C–H···O blue-shifting hydrogen bond is revealed upon complexation of CH₃OH, HCHO, HCOOH, CH₃COCH₃ and HCOOCH₃ with CO₂. Remarkably, existence of weak hydrogen bonded C–H···O interaction is not found in the (CH₃OCH₃, CO₂) and (CH₃NH₂, CO₂) pairs.

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1. Introduction

During the last decades, the nature of interactions of CO₂ with organic and/or inorganic compounds has been the subject of a large amount of experimental and theoretical studies alike [1–3]. Miscibility and dissolution of materials in liquid and supercritical CO₂ (scCO₂) have also attracted much attention due to the advantages of CO₂ in industrial processes over the more conventional organic solvents, and the many potential applications in ‘green’ chemistry [4]. It turns out that although CO₂ is a green-house gas, it is regarded as an environmentally benign liquid solvent owing to its fewer hazard. But more importantly, it is an attractive alternative solvent due to the ease of solvent removal, its abundance, low cost, and tunability of solvent parameters [5]. Accordingly, scCO₂ has been widely used in several chemical processes such as extraction, separation, chemical reaction and material processing [6,7]. Recently, direct sol–gel reactions in scCO₂ have been used in the synthesis of oxide nanomaterials, oligomers and polymers [8–10].

Due to the lack of polarity and a dipole moment, scCO₂ is a poor solvent for most polar solutes [11]. However, the CO₂ molecule possesses a substantial quadrupole moment and a polar >C=O bond, making the majority of materials bearing carbonyl functional or fluoride groups soluble in scCO₂ [12]. A great effort has thus been dedicated to the enhancement in applicability of CO₂ as a solvent through the use of ‘CO₂-philes’. The latter can be incorporated into the structure of insoluble or poorly soluble materials, making them soluble in CO₂ at workable level of low temperatures and

pressures [13]. Numerous CO₂-philes were reported during the 1990s [14,15]. Most of them are fluorocarbon-based CO₂-philes exhibiting high solubility in scCO₂ [16–18]. However the latter materials are expensive, economically unfavorable and also environmentally unfriendly. Therefore, interest in the development of environmentally benign, nonfluorous and inexpensive CO₂-philic materials remains strong. In addition, although many theories on the nature of interactions involving in this process have been put forward, the debate is still continuing.

Up to now, a large number of complexes of some small organic molecules with CO₂ have been reported [16,19–25]. These results pointed toward the presence of a Lewis acid–base (LA–LB) type of interaction in which both carbon and oxygen of CO₂ play the role of the respective electron acceptor and donor centers. Furthermore, some of the investigated systems also suggest the existence of a weak C–H···O hydrogen bonded (HB) interaction. Rivelino, Kim and co-workers [20,21] thus reported that the C–H···O HB contact likely acts as an additional interaction along with a main contribution of the LA–LB interaction in stabilizing the complexes of HCHO, CH₃CHO and CH₃COOCH₃ with CO₂. Nevertheless, the specific role of the C–H···O HB interaction in enhancing solubility remains questionable. Additionally, the origin of the blue shifting hydrogen bond is still not well understood despite the fact that in previous studies several rationalizations have been offered [26–30].

In more recent investigations, the LA–LB interaction between CO₂ and some carbonyl-functionalized compounds has been analyzed [21,22,28–32]. The strongest evidence for C–H···O interaction was put forward by Wallen et al. [19,33–35]. It is however obvious that more systematic studies are required to unravel the origin of interactions, rather than considering the results taken

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from a few disparate systems. Motivated by the importance of CO₂, we set out to investigate in the present Letter its interactions with some typical organic molecules including methanol (CH₃OH), methylamine (CH₃NH₂), formaldehyde (HCHO), formic acid (HCOOH), dimethylether (CH₃OCH₃), acetone (CH₃COCH₃) and methyl formate (HCOOCH₃). These represent the simplest members of different functional groups and contain C–H bonds. To the best of our knowledge, a systematic investigation of these complexes has not been available in the literature. In addition, our purpose is also to further probe the existence of LA–LB interaction, or both LA–LB and HB interactions, and their mutual effects on the strength of the complexes investigated. We also aim at identifying the inherent C–H···O hydrogen bond. The differences in lone pair electron densities and structural features in affecting the complex strength allow us to probe the question of how the solubility in scCO₂ will be changed with respect to the functionalized groups.

2. Computational methods

Geometrical parameters of all the monomers and complexes are optimized without symmetry constraint using the MP2/aug-cc-pVTZ level of theory. Harmonic vibrational frequencies are also calculated at this level to ensure that the optimized structures are local minima on the potential energy surfaces, and to estimate their zero-point energies (ZPE). In order to avoid vibrational coupling between the CH₂ and CH₃ stretching modes in HCHO and CH₃COCH₃, respectively, harmonic frequencies are calculated in the DCHO and CHD₂COCH₃ isotopomers for both monomers and complexes. Interaction energies of the complexes investigated are determined using the supermolecule approach as the difference in total energies between that of each complex and the sum of relevant monomers.

The depth of the potential energy for the complexes and isolated monomers are further evaluated using single-point electronic energy calculations at CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ. Basis set superposition errors (BSSE) are also estimated using the counterpoise procedure of Boys and Bernardi [36] for CCSD(T) energies. All quantum chemical calculations mentioned above are carried out by the GAUSSIAN 09 program package [37]. Topological properties of electron density are probed using the AIM 2000 [38] software for the atom-in-molecule (AIM) theory [39]. Natural bond orbital (NBO) analysis is also performed using of the GENNBO 5.G program [40] at the MP2/aug-cc-pVTZ level.

3. Results and discussion

3.1. Geometric structures and AIM analyses

The shape, symmetry point group and selected geometric parameters of the stable complexes (denoted hereafter by letters and numbers **XY** with **X** = A, B, C, ... and **Y** = 1, 2, 3, ...) formed from interactions between the host molecules CH₃OH, CH₃NH₂, HCHO, HCOOH, CH₃OCH₃, CH₃COCH₃ and HCOOCH₃, and the guest molecule CO₂ are presented in Figure 1. Changes of C=O bond lengths in CO₂ computed at the MP2/aug-cc-pVTZ level upon complexation are tabulated in Table 1.

In all systems considered, there are O···C or N···C intermolecular contacts, in which O and N atoms belong to the host molecules and C atom to CO₂, except for the geometry **C2** which only has the C–H···O contact. CO₂ geometry is marginally bent in most of obtained systems, except for that of **C2** (Figure 1). These marginal deviations from linearity (180°) are caused by a small distortion of carbon atom from sp-hybridization. Furthermore, there is also a differentiated change of C=O bond lengths in CO₂ upon complex formation (cf. Table 1). The H···O(CO₂) distances in **A1**, **C1**, **D1**, **D2**,

D3, **F1** and **G1** are smaller or close to the sum of van de Waals radii of H and O atoms (2.72 Å), indicating roughly the existence of HB contacts. This is further supported by the deviations from 180° of ∠OCO angle in CO₂ and the other variations of C=O bond lengths as stated above. On the contrary, no existence of C–H···O HB interactions in **B1**, **C2**, **E1**, **G2** and **G3** could be noted since the H···O(CO₂) distances in these geometries are larger than the sum of van der Waals radii of both H and O atoms.

We now examine the presence of LA–LB interaction in the complexes. All O3···C6, O4···C6, O9···C6 and N2···C6 contact distances seen in Figure 1 are smaller than the sums of van der Waals radii of two relevant atoms (3.22 Å for the O···C one and 3.25 Å for the N···C one). These values obviously suggest the LA–LB interactions when the O···C and N···C atoms encounter each other, in which the electron donor is the O or N atom of the host molecule, and the C center of CO₂ acts as an electron acceptor.

HB and LA–LB interactions can be identified on the basis of the maps of total electron density given in Figure S1 of Supplementary Information (SI). In an attempt to further illustrate presence and strength of both types of interactions, a topological analysis is also carried out by means of the AIM theory at the MP2/aug-cc-pVTZ level. Topological geometries of bond critical points (BCPs) and ring critical points (RCPs) are shown in Figure 2. Electron density ($\rho(r)$) and Laplacian ($\nabla^2(\rho(r))$) values of these critical points in the complexes considered are given in Table S1 of SI. It is worth noting that the BCPs of the C–H···O(CO₂) contact in **B1**, **E1**, **G2** and **G3** are not observed, indicating the non-existence of these HB interactions (Figure 2). This represents a viewpoint on the non-presence of the C–H···O HB interaction in stabilizing **E1** when CH₃OCH₃ interacting with CO₂, which is different from the previous prediction of Kim and Kim [21]. These authors suggested the existence of the C–H···O weak hydrogen bond acting as a cooperative interaction along with LA–LB interaction in strength enhancement of **E1** although the H···O distance is estimated to be 2.92 Å at the MP2/aug-cc-pVDZ level, significantly larger than the sum of van der Waals radii of both atoms (2.72 Å). Following complexation, the presence of BCPs of C–H···O(CO₂) contacts is found in structures **A1**, **C1**, **C2**, **D2**, **D3**, **F1** and **G1**. On the other hand, BCP of the O–H···O(CO₂) contact is also observed in **D1**. Similarly, the BCPs of the C–N···C(CO₂) contact are also found in **B1**, and C=O···C(CO₂) contacts in **A1**, **C1**, **C2**, **D1**, **D2**, **D3**, **E1**, **F1**, **F2**, **G1** and **G3**. As shown in Table S1 of SI, all the $\rho(r)$ and $\nabla^2(\rho(r))$ values of BCPs of the above-mentioned contacts fall within the critical limit for formation of non-covalence interactions [41]. As a consequence, the C–H···O(CO₂) and O–H···O(CO₂) contacts, and the C–N···C(CO₂) and C=O···C(CO₂) ones can be considered as HB and LA–LB interactions, respectively. Besides, in **G2**, a C···O(CO₂) quite weak interaction is detected, whereas a C–H···O(CO₂) hydrogen bond is not attained. Our calculations also indicate the existence of a ring structure characterized by one ring critical point (yellow small sphere) in some of examined complexes such as **A1**, **C1**, **C2**, **D1**, **D2**, **D3**, **F1**, **G1** and **G2**.

Remarkably, a very large electron density of 0.0186 a.u. at BCP of the O–H···O contact in **D1** is obtained, which is also larger than the maximum electron density value of 0.0145 a.u. at BCP of the C=O···C contact in **E1**, as compared to those found in all remaining complexes. Furthermore, it is twice as large as the maximum electron density of 0.0085 a.u. at BCP of the C–H···O interaction. Consequently, the strength of **D1** arises mainly from the O–H···O hydrogen bond, and also it should be stressed that an O–H···O bond is inherently stronger than a C–H···O bond.

3.2. Interaction energies and NBO analyses

Interaction energies are summarized in Table 2. All interaction energies with and without BSSE corrections are significantly

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