Theoretical Studies for the Supercritical CO_2 Solubility of Organophosphorous Molecules: Lewis Acid-Base Interactions and C–H···O Weak Hydrogen Bonding

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Exploring the basic concepts for the design of CO_2-philic molecules is important due to the possibility for "green" chemistry in supercritical CO_2 as substitute solvent systems. The Lewis acid-base interactions and C–H···O weak hydrogen bonding were suggested as two key factors for the solubility of CO_2-philic molecules. We have performed high level quantum mechanical calculations for the van der Waals complexes of CO_2 with trimethylphosphate and trimethylphosphine oxide, which have long been used for metal extractants in supercritical CO_2 fluid. Structures and energies were calculated using the MP2/6-31+G(d) and recently developed multilevel methods. These studies indicate that the Lewis acid-base interactions have larger impact on the stability of structure than the C–H···O weak hydrogen bonding. The weak hydrogen bonds in trimethylphosphine oxide have an important role to the large supercritical CO_2 solubility when a metal is bound to the oxygen atom of the P=O group. Trimethylphosphate has many Lewis acid-base interaction sites so that it can be dissolved into supercritical CO_2 easily even when it has metal ion on the oxygen atom of the P=O group, which is indispensable for a good extractant.

Key Words : CO_2 solubility, Lewis acid-base interaction, Weak hydrogen bonding, Multilevel calculations, Supercritical CO_2

Introduction

The theoretical and experimental studies for the supercritical carbon dioxide (sc-CO_2) have been performed extensively.[1-4] sc-CO_2 has many advantages as a process solvent, in that it is inexpensive, abundant, and environmentally genial. As a result, for the past decade, sc-CO_2 has been treated as the "green" processing solvent. The usage of sc-CO_2 as a solvent has serious limitations due to the poor solubility of the majority of polar and ionic materials. To this end, it was hypothesized that polar materials could be added to the solution via various surfactants. Supercritical fluid extraction (SFE) using sc-CO_2 with a surfactant instead of an organic solvent has recently been established as an advanced method for separation of metals from liquid or even from solid samples. Applications of SFE include the separation of metal ions such as uranium(VI) and fission product elements from nitric acid solution into supercritical CO_2 containing an organophosphorus surfactant such as tributylphosphate (TBP).[5,6] The solubility of organophosphine oxides[7,8] in sc-CO_2 along with various organic molecules has also been studied to evaluate the applicability of surfactant in SFE and to design a new surfactant feasible to SFE of a metal ion. Determination of surfactant solubility into sc-CO_2 is indispensable from both fundamental and practical viewpoints. Generally solubility of a surfactant in sc-CO_2 is so low that it may restrict the preparation of sc-CO_2 mixture containing the surfactant of sufficiently high concentration. Many research groups have tried to design CO_2-philic materials and to increase the solubility of the CO_2-based organic solvent. Therefore it is an important topic to understanding the solubility of CO_2-philic materials for further development of SFE.

Two possible major interactions of CO_2 complexes are Lewis acid-base (LA-LB) interaction and the C–H···O weak hydrogen bonding. Although the dipole moment for carbon dioxide is zero, the quadrupole moment is not. It is obvious that there is charge separation between carbon and oxygen atoms, so the polarized electron density moves more toward the oxygen atoms. As a result, the carbon atom has a partial positive charge acting as a Lewis acid (LA) and the two oxygen atoms have partial negative charges acting as a Lewis base (LB), resulting in the carbon atom acting as an electron acceptor in an LA-LB interaction with carbonyl groups. The oxygen atoms with partial negative charges can be involved in weak electrostatic interactions with properly placed electron-deficient C–H bonds, which form a weak hydrogen bond (H-bond). Recently a number of groups have performed quantum mechanical calculations to estimate the energies of the LA-LB interactions and the weak H-bonds.

Beckman and coworkers[9] have performed extensive quantum mechanical calculation for the CO_2-methyl acetate complex and found that the binding energies for CO_2 interacting with the ether oxygen are very close to those with the carbonyl oxygen. They suggested that ether oxygens should be just as effective as carbonyl oxygens at increasing the solubility of polymers in CO_2. Raveendran and Wallen[10] have studied the role of a cooperative C–H···O interaction as an additional stabilizing interaction along with the LA-LB interaction between CO_2 and carbonyl compounds. It has been well established that the C–H···O weak H-bonds play an important role in structure chemistry and crystal packing,[11-15] in molecular recognition processes,[16,17] and possibly in the structure of biological macromolecules.[12,18-20] Additionally, it is important to investigate whether the CO_2

oxygen atoms can form a weak H-bond with electron-deficient hydrogen atoms in a CO_2-phile. Raveendran and Wallen's *ab initio* calculations have shown that the CO_2 oxygen participates in a cooperative C–H···O H-bond with the electron-deficient hydrogen atoms that are attached to the carbonyl carbon atoms.[10,21,22] NMR, IR and Raman spectroscopic studies of acetaldehyde and CO_2 mixtures provided experimental evidence for the presence of both the LA-LB interaction between CO_2 and the carbonyl group as well as a weak C–H···O H-bond.[21,23] Although the cooperative C–H···O H-bond is formed with CO_2, its role for the enhanced solubility is not certain yet.[9] Recently detailed and systematic studies have been performed to elucidate the role of the weak hydrogen bonding to the sc-CO_2 solubility.[24]

Most of the electronic structure calculations for complexes use a supermolecular approach where the interaction energy of the complex is obtained as the energy difference between the complex and monomers. However, this approach is sensitive to the basis set superposition error (BSSE). In some cases where the interaction energies are small, the BSSEs are as large as the interaction energies.[9,25] A conceptually simple way of accounting for BSSE is the counterpoise correction (CP) method, in which the energies of the fragments are calculated on the full basis of the complex, and these CP-corrected energies are used for the energies of the fragments when computing the interaction energy. However it sometimes overestimates the actual correction.[26-28] Recently, Truhlar and coworkers have suggested elaborate schemes that combine scaling, extrapolation to an infinite basis set, and fitting to a set of experimental data.[29-33] In these methods, the total energy is written as a linear combination of energy terms with different basis sets, and coefficients are adjusted to fit experimental data (atomization energies). The BSSE correction is included in some of the coefficients, although not completely.[34] These linear combination methods are called multilevel methods, and some multilevel methods show very good agreement with experiments of the interaction energies of water and HF dimers.[35]

Organophosphorus reagents such as tributylphosphate and tributylphosphine oxide have long been used as extractants for actinide elements,[36] and, these compounds have also been used in supercritical CO_2 extraction of U and Th from solid and liquid matrices.[7] The LA-LB interactions and weak hydrogen bonding between CO_2 and organophosphorus molecules might also be very important for the sc-CO_2 solubility. We have performed a systematic study to estimate the strength of the LA-LB interaction and the weak C–H···O H-bond in organophosphorus compound using high-level quantum mechanical method and investigated the role of C–H···O H-bonds as a CO_2-philic stabilization factor. We have chosen to study the interaction of two organophosphorus molecules with CO_2, namely, trimethylphosphine oxide (TPO), and trimethylphosphate (TPA).

Computational Methods

All *ab initio* electronic structure calculations were performed using the Gaussian03 pakages.[37] Geometry optimization was performed at the MP2 level using the 6-31+G(d) basis set. The vibrational frequencies were also calculated to confirm that the structures were at the real potential energy minimum. The interaction energies (ΔE) of these complexes are defined as

$$\Delta E = E_{AB} - (E_A + E_B) \tag{1}$$

where E_{AB} is the energy of the optimized CO_2-complex, and E_A, E_B represent the energies of the optimized monomers. The BSSEs were calculated using the CP method of Boys and Bernadi.[38]

$$E_{BSSE} = [E_m(M_1) - E_d(M_1')] + [E_m(M_2) - E_d(M_2')] + E_{rel} \tag{2}$$

$$E_{rel} = [E_m(M_1') - E_m(M_1)] + [E_m(M_2') - E_m(M_2)] \tag{3}$$

where $E_m(M)$ and $E_d(M')$ are the energies of the monomer in its own basis set and in the basis set of the CO_2-complex, respectively. The M and M' indicate the optimized geometry of the monomer and the monomer in the optimized complex, respectively. The fragment relaxation energy (E_{rel}), the energy associated with the transition from the optimized geometry of monomer to the geometry which the monomer has in the complex, should be also included in the BSSE correction. The corrected interaction energy is determined as follows:

$$E_{corr} = E_d(D) - [E_m(M_1) + E_m(M_2)] + E_{BSSE} \tag{4}$$

$$= E_d(D) - [\,E_d(M_1') + E_d(M_2')] + E_{rel} \tag{5}$$

where $E_d(D)$ is the energy of the CO_2-complex in its own basis set. The binding energy (BE) or dissociation energy is defined as the negative value of the interaction energy of the complexes.

The multicoefficient correlated quantum mechanical methods (MCCMs) were used to calculate interaction energies of the complexes. This method has been described elsewhere in detail[29-33] and only a short description of each method employed will be provided. These methods involve differences between energies at different basis sets and theory levels, and a short notation has been used to concisely write the equation for a multilevel energy. In this notation, the pipe "|" is used to represent the energy difference either between two one-electron basis sets $B1$ and $B2$ or between two levels of electronic structure theory $L1$ and $L2$. The energy difference between two basis sets is denoted as

$$\Delta E(L/B2|B1) = E(L/B2) - E(L/B1) \tag{6}$$

where L is a particular electronic structure method, and $B1$ is smaller than $B2$. The energy change that occurs upon improving the treatment of the correlation energy is represented by

$$\Delta E(L2|L1/B) = E(L2/B) - E(L1/B) \tag{7}$$

where $L1$ is a lower level of theory than $L2$, and B is a common one-electron basis set. Finally, the change in energy increment due to increasing the level of the treatment of the correlation energy with one basis set as compared to the

increment obtained with a smaller basis set is represented as

$$\Delta E(L2|L1/B2|B1) = E(L2/B2) - E(L1/B2) - [E(L2/B1) - E(L1/B1)] \quad (8)$$

The Utah form of MCCM methods are written as

$$E(\text{MCCM-UT-L}) = c_1E(\text{HF/cc-pVDZ}) + c_2\Delta E(\text{HF/cc-pVTZ|cc-pVDZ}) + c_3\Delta E(\text{MP2|HF/cc-pVDZ}) + c_4\Delta E(\text{MP2|HF/cc-pVTZ|cc-pVDZ}) + c_5\Delta E(\text{L|MP2/cc-pVDZ}) + E_{SO} + E_{CC} \quad (9)$$

where E_{SO} and E_{CC} represent the spin-orbit and core-correlation energies, respectively, and L=CCSD for the MCCM-UT-CCSD method. The multi-coefficient G3(MCG3) method is written as

$$E(\text{MCG3}) = c_1E(\text{HF/6-31G(d)}) + c_2\Delta E(\text{HF/MG3|6-31G(d)}) + c_3\Delta E(\text{MP2|HF/6-31G(d)}) + c_4\Delta E(\text{MP2|HF/MG3|6-31G(d)}) + c_5\Delta E(\text{MP4SDQ|MP2/6-31G(d)}) + c_6\Delta E(\text{MP4SDQ|MP2/6-31G(2df,p)|6-31G(d)}) + c_7\Delta E(\text{MP4|MP4SDQ/6-31G(d)}) + c_8\Delta E(\text{QCISD(T)|MP4/ 6-31G(d)}) + E_{SO} + E_{CC} \quad (10)$$

The multilevel energies are calculated by using the MULTILEVEL 4.0 program.[39] This program uses the Gaussian03 packages to obtain the energy, gradient, and Hessians components and then combines the components to calculate the multilevel energy, gradient, and Hessians.

Results and Discussion

The solubility of organic molecules in sc-CO_2 fluid depends on the interactions between CO_2 and the CO_2-philic functional group, and their relative strength compared to the solvent-solvent, and solute-solute interactions as well. The structure and binding energies of the CO_2 dimer have been extensively studied.[40-44] It is well established that there are two minimum energy conformations for the CO_2 dimer; slipped parallel (C_{2h} symmetry) and T-shaped (C_{2v} symmetry). In the gas phase the CO_2 dimer with the slipped parallel geometry is preferred. Tsuzuki and coworkers[44] have reported that the binding energies of the CO_2 dimer with the slipped parallel and T-geometries are 1.36 and 1.14 kcal/mol, respectively, at the MP2 level with the complete basis sets. The CO_2 complexes that have an important role to the sc-CO_2 solubility should have larger binding energies than these values. The C–H···O weak hydrogen bonding is well-established in structural chemistry[11,12,16] and recently reported to have an important role in biological processes.[18-20] The weak hydrogen bonding is expected to be very weak. However its energy should be larger than the van der Waals energy between CO_2 and non-polar molecules, such as methane and ethane in order for it to be meaningful in the sc-CO_2 solubility. Binding energies between CO_2 and hydrocarbons, such as methane and ethane, have been calculated by Diep *et al.*[25] at the MP2/aug-cc-pVTZ level with the BSSE correction, which are 0.88 and 1.17 kcal/mol, respectively. Recently, Raveendran and Wallen[45] have also reported that the binding energy of CH_4-CO_2 complex is 0.87 kcal/mol at the MP2/aug-cc-pVQZ level with the CP-correction. The CP-correction often overestimates the BSSE,[26-28] which may lead an incorrect conclusion, particularly when the binding energies are very small. Recent MCCM calculations with good empirical parameters and without the CP correction have reproduced dimerization energies for $(H_2O)_2$ and $(HF)_2$ within chemical accuracy.[34,35] Multilevel methods have recently been used to calculate the binding energies for the structure of CO_2-CH_4 complex, and the results are listed in Table 1.[24] The BSSE using the CP-correction is much larger than the binding energy including ZPEs at the MP2/aug-cc-pVDZ level. The MP2/aug-cc-pVQZ energy is 0.92 kcal/mol without the ZPE corrections, which is practically the same as the MCCM-UT-CCSD value. The best estimates of the van der Waals energy for the CH_4-CO_2 complex were 0.66 and 1.12 kcal/mol with and without ZPE corrections at the MCCM-CO-CCSD(T) level, respectively. The later is slightly smaller than the binding energy of the slipped-parallel CO_2 dimer but similar to that of the T-shaped dimer. The optimized structure for the CH_4-CO_2 complex at the MP2/aug-cc-pVDZ level is depicted in Figure 1. The distances between O and hydrogen atoms are in the range of 3 and 3.2 Å.

Table 1. Binding Energies for the CO_2-Methane Complex Calculated at the MP2, MCCM-UT-CCSD, MCCM-CO-CCSD(T) and MCG3 levels[a]

	Energies
MP2/aug-cc-pVDZ	0.62(0.16) /0.76[b]
MP2/aug-cc-pVTZ	0.88/0.19
MP2/aug-cc-pVQZ//MP2/aug-cc-pVDZ	0.92(0.45) /0.14, 0.87[d]
MCCM-UT-CCSD//MP2/aug-cc-pVDZ	0.93(0.46)
MCCM-CO-CCSD(T) //MP2/aug-cc-pVDZ	1.12(0.66)
MCG3//MP2/aug-cc-pVDZ	0.86(0.39)

[a]Energies in kcal/mol. Numbers in parenthesis are with ZPE corrections at the MP2/aug-cc-pVDZ level.[24] [b]The BSSE using the CP correction. [c]Ref. 25. [d]Ref. 45

Three CO_2 complexes with trimethylphosphine oxide (TPO) have been calculated, and the optimized structure and binding energies are shown in Figure 2 and Table 2, respectively. In the TPO-A complex the CO_2 molecule is bound to the phosphinyl oxygen (P=O) and two methyl protons, and in TPO-B it is bound to three methyl protons only. The P=O···C distance and the weak H-bond distances in TPO-A are 2.73 and 2.79 Å, respectively. The shorter H-bond distances

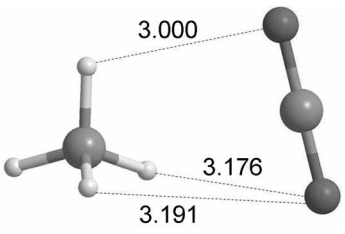

Figure 1. Geometric parameters for CO_2-CH_4 complex at the MP2/aug-cc-pVDZ level.

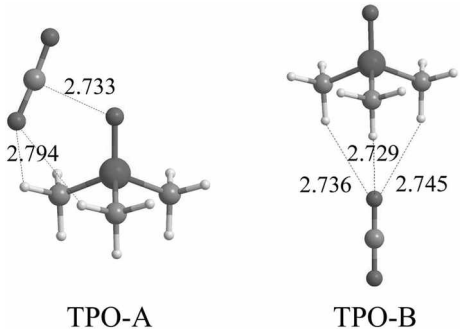

Figure 2. The optimized structures of CO_2-timethylphosphine oxide complexes at the MP2/6-31+G(d) level.

Table 2. Binding Energies for the CO_2-Trimethylphosphine Oxide (TPO) Complexes Calculated at the MP2, MCCM-UT-CCSD and MCG3 levels [a]

	TPO-A	TPO-B
MP2/6-31+G*	3.64(3.06)/2.14[b]	1.17(0.81)/1.00
MCCM-UT-CCSD	5.30(4.71)	1.50(1.14)
MCG3	5.43(4.84)	2.07(1.71)

[a]Energies in kcal/mol. Numbers in parenthesis are with ZPE corrections. [b]The BSSE using the CP correction

in TPO-B compared with those of TPO-A, suggest that this type of weak H-bond is stronger. The binding energies for TPO-A and TPO-B at the MP2 level are 3.64 and 1.17 kcal/mol before the ZPE correction and 3.06 and 0.81 kcal/mol after the correction, respectively. The BSSEs, which should be considered in the calculation of the binding energies of complexes, are 2.14 kcal/mol for TPO-A, and 1.0 kcal/mol for TPO-B. These values are comparable with the binding energies of corresponding complexes including ZPEs. Fragment relaxation energies, which are part of the BSSE corrections, are negligible in most cases, so not listed in this table. The LA-LB interaction energy at the MCCM-UT-CCSD level is 4.7 kcal/mol with ZPE corrections, which is larger than those for the carbonyl or ether oxygen bound CO_2 complexes, which are about 2.4 and 3.7 kcal/mol, respectively.[24] These results indicate that the solvent quadrupole-solute dipole interaction of CO_2 with the P=O group is larger than those with the C=O and ether groups. The weak H-bond energy of TPO-B is about 2 kcal/mol, which is much larger than the van der Waals energy of CO_2-CH_4 complex. This weak H-bond is much stronger than those of carbonyl or ether containing complexes such as CO_2-methylacetate, CO_2-acetaldehyde, and CO_2-dimethylether. Such strong C–H···O bond may results in a specific solvent-solute interaction in a sc-CO_2 solution that can increase the solubility. When a metal is coordinated to the oxygen atom of TPO for the extraction, then there will be no LA-LB interaction with CO_2. The large binding energy of the weak H-bond seems to make the metal binding TPO soluble in sc-CO_2, which is indispensable for a good extractant.

Three complexes of trimethylphosphate (TPA) were calculated depending on the location of the CO_2 molecule, and their structures and energies are shown in Figure 3 and Table

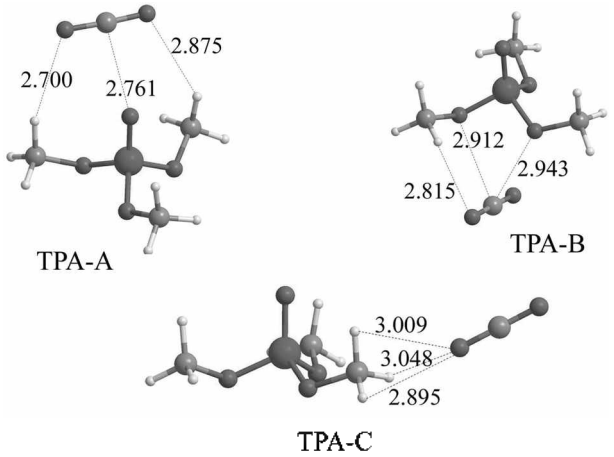

Figure 3. The optimized structures of CO_2-timethylphosphate complexes at the MP2/6-31+G(d) level.

Table 3. Binding Energies for the CO_2-Trimethylphosphate (TPA) Complexes Calculated at the MP2, MCCM-UT-CCSD and MCG3 levels [a]

	TPA-A	TPA-B	TPA-C
MP2/6-31+G*	2.87(2.33)/2.28[b]	2.11(1.57)/3.67	0.68(0.43)/0.69
MCCM-UT-CCSD	3.79(3.26)	2.99(2.45)	0.36(0.11)
MCG3	4.51(3.97)	4.11(3.57)	1.05(0.80)

[a]Energies in kcal/mol. Numbers in parenthesis are with ZPE corrections. [b]The BSSE using the CP correction

3, respectively. In TPA-A and TPA-B complexes, the CO_2 molecule is bound to the P=O and methoxy-oxygen atoms, respectively, and in TPA-C to the methyl protons. The P=O ···C distance of TPA-A is longer than the corresponding distances of TPO-A, but shorter than the C=O···C distance in CO_2-methylacetate complex (2.87 Å).[10] These results suggest that the LA-LB interaction of TPA-A is weaker and stronger than those of TPO-A and CO_2-methylacetate, respectively. The binding energies for TPA-A, TPA-B and TPA-C at the MP2 level are 2.33, 1.57 and 0.43 kcal/mol with the ZPE corrections, respectively. The BSSEs are quite large compared to the binding energies of corresponding complexes including ZPEs. The average binding energy of TPA-A from two multilevel methods is 3.6 kcal/mol including ZPEs, which is smaller than that of TPO-A. However this value is larger than the corresponding value of the CO_2-methylacetate complex, which is 2.9 kcal/mol.[24] The average binding energy including ZPEs originated from the LA-LB interaction with methoxy-oxygen in TPA-B (2.9 kcal/mol) is similar to that of CO_2-methylacetate complex (3.0 kcal/mol), and the weak H-bond energy in TPA-C is also similar to that of CO_2-dimethylether complex.[24] Although the LA-LB interaction in the TPA complexes is weaker than that of TPO complex, TPA has an important advantage over TPO as a good extractant. TPA has more sites for LA-LB interaction so that it can have still large sc-CO_2 solubility even with a metal ion bound to the P=O group. These two types of LA-LB interaction in trimethylphosphate, which have fairly large binding energies, attribute to the large sc-

CO_2 solubility of tri-*n*-butylphosphate that have long been used in sc-CO_2 extraction.

Conclusions

We have investigated the LA-LB interaction and weak H-bonds in organophosphorus compounds, namely, trimethylphosphine oxide (TPO) and trimethylphosphate (TPA), which have long been used for metal extractants in supercritical CO_2 fluid. The LA-LB interaction energy is much larger than the weak H-bond energy, thus it would the main driving force for the large sc-CO_2 solubility. The LA-LB interaction energies between CO_2 and the P=O group are quite large, *i.e.*, 4.7 and 3.6 kcal/mol for TPO and TPA including zero-point energies, respectively. The binding energy for the C–H···O weak H-bond in TPO is also quite large compared to the CO_2-CH_4 van der Waals energy and the dimerization energy of CO_2, which results in the large sc-CO_2 solubility for the metal binding TPO at the oxygen atom. The LA-LB interaction energy and the binding energy of C–H···O weak H-bond for TPA are smaller than those for TPO. However TPA has more binding sites for LA-LB interactions so that it can be dissolved into sc-CO_2 easily even when it has metal ion on the oxygen atom of the P=O group, which is indispensable for a good extractant.

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