

Theoretical Studies for the Supercritical CO₂ 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 CO₂-philic molecules is important due to the possibility for “green” chemistry in supercritical CO₂ 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 CO₂-philic molecules. We have performed high level quantum mechanical calculations for the van der Waals complexes of CO₂ with trimethylphosphate and trimethylphosphine oxide, which have long been used for metal extractants in supercritical CO₂ 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 CO₂ 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 CO₂ 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 : CO₂ solubility, Lewis acid-base interaction, Weak hydrogen bonding, Multilevel calculations, Supercritical CO₂

Introduction

The theoretical and experimental studies for the supercritical carbon dioxide (sc-CO₂) have been performed extensively.¹⁻⁴ sc-CO₂ has many advantages as a process solvent, in that it is inexpensive, abundant, and environmentally genial. As a result, for the past decade, sc-CO₂ has been treated as the “green” processing solvent. The usage of sc-CO₂ 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-CO₂ 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 CO₂ containing an organophosphorus surfactant such as tributylphosphate (TBP).^{5,6} The solubility of organophosphine oxides^{7,8} in sc-CO₂ 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-CO₂ is indispensable from both fundamental and practical viewpoints. Generally solubility of a surfactant in sc-CO₂ is so low that it may restrict the preparation of sc-CO₂ mixture containing the surfactant of sufficiently high concentration. Many research groups have tried to design CO₂-philic materials and to increase the solubility of the CO₂-based organic solvent. Therefore it is an important topic to understanding the solubility of CO₂-philic materials for further development of SFE.

Two possible major interactions of CO₂ 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 coworkers⁹ have performed extensive quantum mechanical calculation for the CO₂-methyl acetate complex and found that the binding energies for CO₂ 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 CO₂. Raveendran and Wallen¹⁰ have studied the role of a cooperative C–H···O interaction as an additional stabilizing interaction along with the LA-LB interaction between CO₂ 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 CO₂

oxygen atoms can form a weak H-bond with electron-deficient hydrogen atoms in a CO₂-phile. Raveendran and Wallen's *ab initio* calculations have shown that the CO₂ 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 CO₂ mixtures provided experimental evidence for the presence of both the LA-LB interaction between CO₂ 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 CO₂, 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-CO₂ 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 CO₂ extraction of U and Th from solid and liquid matrices.⁷ The LA-LB interactions and weak hydrogen bonding between CO₂ and organophosphorus molecules might also be very important for the sc-CO₂ 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 CO₂-philic stabilization factor. We have chosen to study the interaction of two organophosphorus molecules with CO₂, namely, trimethylphosphine oxide (TPO), and trimethylphosphate (TPA).

Computational Methods

All *ab initio* electronic structure calculations were per-

formed using the Gaussian03 packages.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

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

where E_{AB} is the energy of the optimized CO₂-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

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

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

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 CO₂-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:

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

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

where $E_d(D)$ is the energy of the CO₂-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 detail²⁹⁻³³ 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

$$\Delta E(L/B2|B1) = E(L/B2) - E(L/B1) \quad (6)$$

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

$$\Delta E(L2|L1/B) = E(L2/B) - E(L1/B) \quad (7)$$

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

$$E(\text{MCCM-UT-L}) = c_1 E(\text{HF/cc-pVDZ}) + c_2 \Delta E(\text{HF/cc-pVTZ}|\text{cc-pVDZ}) + c_3 \Delta E(\text{MP2}|\text{HF/cc-pVDZ}) + c_4 \Delta E(\text{MP2}|\text{HF/cc-pVTZ}|\text{cc-pVDZ}) + c_5 \Delta E(\text{L}|\text{MP2/cc-pVDZ}) + E_{\text{SO}} + E_{\text{CC}} \quad (9)$$

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

$$E(\text{MCG3}) = c_1 E(\text{HF}/6\text{-}31\text{G}(\text{d})) + c_2 \Delta E(\text{HF}/\text{MG3}|\text{6-}31\text{G}(\text{d})) + c_3 \Delta E(\text{MP2}|\text{HF}/\text{6-}31\text{G}(\text{d})) + c_4 \Delta E(\text{MP2}|\text{HF}/\text{MG3}|\text{6-}31\text{G}(\text{d})) + c_5 \Delta E(\text{MP4SDQ}|\text{MP2}/\text{6-}31\text{G}(\text{d})) + c_6 \Delta E(\text{MP4SDQ}|\text{MP2}/\text{6-}31\text{G}(\text{2df,p})|\text{6-}31\text{G}(\text{d})) + c_7 \Delta E(\text{MP4}|\text{MP4SDQ}/\text{6-}31\text{G}(\text{d})) + c_8 \Delta E(\text{QCISD}(\text{T})|\text{MP4}/\text{6-}31\text{G}(\text{d})) + E_{\text{SO}} + E_{\text{CC}} \quad (10)$$

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-CO₂ fluid depends on the interactions between CO₂ and the CO₂-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 CO₂ dimer have been extensively studied.⁴⁰⁻⁴⁴ It is well established that there are two minimum energy conformations for the CO₂ dimer; slipped parallel (C_{2h} symmetry) and T-shaped (C_{2v} symmetry). In the gas phase the CO₂ dimer with the slipped parallel geometry is preferred. Tsuzuki and coworkers⁴⁴ have reported that the binding energies of the CO₂ 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 CO₂ complexes that have an important role to the sc-CO₂ 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 CO₂ and non-polar molecules, such as methane and ethane in order for it to be meaningful in the sc-CO₂ solubility. Binding energies between CO₂ 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 Wallen⁴⁵ have also report-

Table 1. Binding Energies for the CO₂-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 ^c	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)

^aEnergies in kcal/mol. Numbers in parenthesis are with ZPE corrections at the MP2/aug-cc-pVDZ level.²⁴ ^bThe BSSE using the CP correction.⁴⁵ ^cRef. 25. ^dRef. 45

ed that the binding energy of CH₄-CO₂ 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 (H₂O)₂ and (HF)₂ within chemical accuracy.^{34,35} Multilevel methods have recently been used to calculate the binding energies for the structure of CO₂-CH₄ 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 CH₄-CO₂ 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 CO₂ dimer but similar to that of the T-shaped dimer. The optimized structure for the CH₄-CO₂ 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.

Three CO₂ 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 CO₂ 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

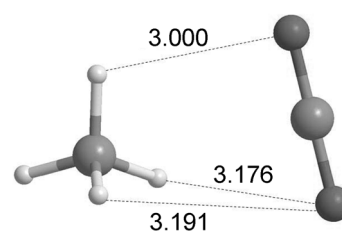


Figure 1. Geometric parameters for CO₂-CH₄ complex at the MP2/aug-cc-pVDZ level.

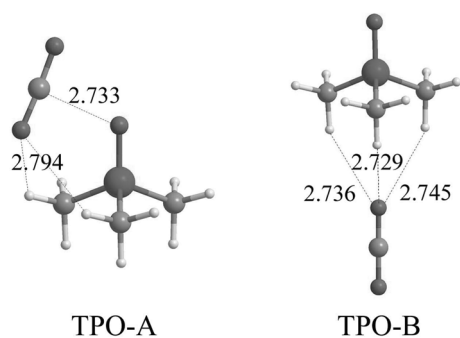


Figure 2. The optimized structures of CO₂-trimethylphosphine oxide complexes at the MP2/6-31+G(d) level.

Table 2. Binding Energies for the CO₂-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)

^aEnergies in kcal/mol. Numbers in parenthesis are with ZPE corrections.

^bThe 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 CO₂ complexes, which are about 2.4 and 3.7 kcal/mol, respectively.²⁴ These results indicate that the solvent quadrupole-solute dipole interaction of CO₂ 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 CO₂-CH₄ complex. This weak H-bond is much stronger than those of carbonyl or ether containing complexes such as CO₂-methylacetate, CO₂-acetaldehyde, and CO₂-dimethylether. Such strong C-H...O bond may result in a specific solvent-solute interaction in a sc-CO₂ 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 CO₂. The large binding energy of the weak H-bond seems to make the metal binding TPO soluble in sc-CO₂, which is indispensable for a good extractant.

Three complexes of trimethylphosphate (TPA) were calculated depending on the location of the CO₂ molecule, and their structures and energies are shown in Figure 3 and Table

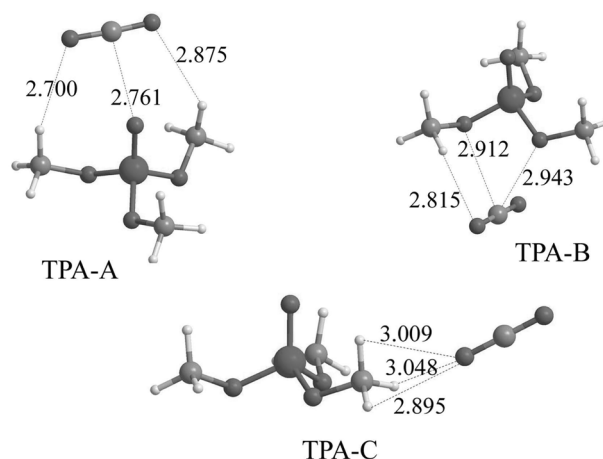


Figure 3. The optimized structures of CO₂-trimethylphosphate complexes at the MP2/6-31+G(d) level.

Table 3. Binding Energies for the CO₂-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)

^aEnergies in kcal/mol. Numbers in parenthesis are with ZPE corrections.

^bThe BSSE using the CP correction

3, respectively. In TPA-A and TPA-B complexes, the CO₂ 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 CO₂-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 CO₂-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 CO₂-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 CO₂-methylacetate complex (3.0 kcal/mol), and the weak H-bond energy in TPA-C is also similar to that of CO₂-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-CO₂ 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-

CO₂ solubility of tri-*n*-butylphosphate that have long been used in sc-CO₂ 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 CO₂ fluid. The LA-LB interaction energy is much larger than the weak H-bond energy, thus it would be the main driving force for the large sc-CO₂ solubility. The LA-LB interaction energies between CO₂ 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 CO₂-CH₄ van der Waals energy and the dimerization energy of CO₂, which results in the large sc-CO₂ 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-CO₂ 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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