

A Theoretical Study of the Stability and Dielectric Constants of Molybdate-Phosphonic Acid Complex

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ABSTRACT

In this work, we investigated the stability of Molybdate-Phosphonic Acid (MPA) complex by density functional theory (DFT) computations in six solvents with the dielectric constant ranging from 1.92 to 10.36. The methods are used for calculations are B3LYP and B3PW91 that have been studied in two series of basis sets: D95** and 6-31+G (d,p) for hydrogen and oxygen atoms; LANL2DZ for Mo and Phosphorus. Considering the effect of solvent, using PCM solvent model, the stability of MPA complex when passing to higher dielectric constants is calculated. Predicted geometry and relative stability are discussed. Equilibrium geometry in the ground electronic state energy has been calculated for 1:1 complex. The best results for energetic and geometrical ground state in different of used solvents were obtained with Becke3LYP calculations. An increasing stabilization of MPA when increasing the dielectric constant in a continuum solvent model.

Keywords: Molybdate; Phosphonic Acid; Solvent Effect; DFT; PCM Model

INTRODUCTION

The complex of transition metal with ligands of oxyacids of phosphorus, such as phosphonic acid, has been the subject of theoretical study. Many natural and artificial supramolecules are formed through intermolecular forces such as hydrogen bonding, Van-Der Waals forces, and hydrophobic interactions [1]. The groups of Elguero [2] and Mó [3,4] as well as other authors have shown the usefulness of the AIM models in interpreting the strength of some simple hydrogen-bonded systems such as methanol-water, phosphonic acid, and phosphinoxides and aminoxides. The accumulation of sufficient experimental data in the last few decades has not only provided an extended picture of the application range of this class of compounds, but has also allowed for some theoretical and mechanistic studies aimed at gaining a deeper understanding of most of the reaction mechanisms involving the diesters of H-phosphonic acid [5]. When solvent effects are taken in to account, the reverse

order is found, in accordance with the experimental data [6, 7]. Usually, systems are polarized by the donor (D) and acceptor (A) substituents, resulting in stronger intramolecular charge transfer and large dipole moment, for example π -conjugated [8].

DFT methods, particularly hybrid functional methods have evolved to a powerful quantum chemical tool for a determination of the electronic structure of molecules. DFT has been widely applied by chemists to study of molecular properties in the past 30 years [9, 10]. In the framework of DFT approach, different exchange and correlation functionals are routinely used [11]. In this paper we have investigated the hypothesis of rationalizations of stabilities of MPA Complex by means of DFT methods. DFT calculations were carried out at the B3LYP [12] and B3PW91 methods with two series of basis

sets: D95** and 6-31+G (d,p) for hydrogen and oxygen atoms; LANL2DZ for Mo and Phosphorus have been carried out. Hydrogen bonding will be discussed in terms of observable properties such as geometrical parameters and interaction energy. A number of significant theoretical and algorithmic advances have been proposed towards incorporating solvent effects into quantum chemical computations [7]. Earlier ab initio studies of the structures and stabilities of hydrogen-bonded assemblies of nucleic acid basis carried out [13] and showed that quantum chemical techniques could now be used to perform calculations on molecular systems of practical significance.

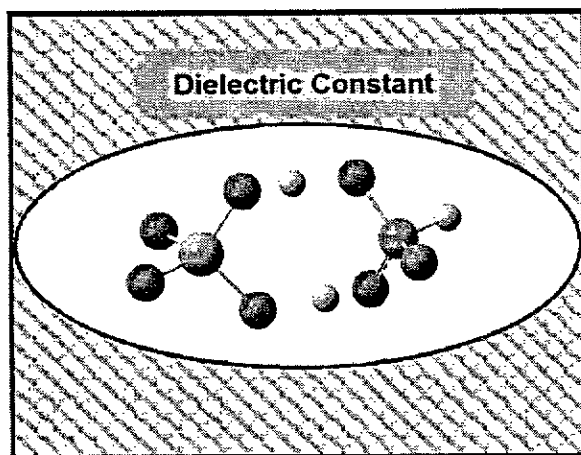


Fig. 1. MPA Complex and PCM Model.

A long-standing problem in theoretical chemistry concerns development and benchmarking of solvation models. Even though quantum chemistry for small isolated molecules has reached the limit of chemical accuracy, the same cannot be said for molecules subjected to an environment, for example, a solute in a solvent. Two different solvation models are available in Gaussian03 – Polarized Continuum Model (PCM) and the Onsager solvation model. Both these methods calculate the energy of a molecule by placing the solute in a cavity and applying a dielectric through it [14, 15] (Figure 1.). The PCM procedure, one of the most widely used continuum dielectric methods [16-18, 24] is applied to study the solvent effects on electronic structures. Geometry optimizations under PCM with Gaussian03 have been possible in comparison with Onsager solvation model up

to 16 heavy atoms (work of Larry Williams). In this approach all the effects of solvent were averaged out by embedding the solute molecule within a dielectric medium to treat the bulk, long-range effect of solvation, but may underestimate local effect introduced by the solvent molecules. The electrostatic model yields a spherically averaged potential, while both the PCM model and the DFT based model provide direction-dependent potentials. As a consequence, when using the PCM model and the DFT-based model, potential curves for electron emission can be obtained for all possible directions [19].

The local dipole-dipole interactions between solute and solvent are significant for MPA in different solvents. In addition, the specific hydrogen bonds are formed in some polar solvents such as DichloroEthane. The solvent properties in the vicinity of the solute (usually called the first solvation shell) may be quite different from the bulk solvents.

COMPUTATIONAL DETAILS

All DFT calculations were carried out with the Gaussian 03 program [20]. Geometry optimizations in the solvent phase for all components and complex were performed at the DFT level with B3LYP and B3PW91 functionals and with two series of basis sets:

- A. Dunning basis set plus polarized functions (D95**) for hydrogen and oxygen atoms; LANL2DZ for Molybdenum and Phosphor. The effective core potential of Wadt and Hay is also included for Mo and P.
- B. Double-zeta valance basis set plus polarized and diffuse functions (6-31+G(d,p)) for hydrogen and oxygen atoms; LANL2DZ for Molybdenum and Phosphor. The effective core potential of Wadt and Hay is also included for Mo and P.

This level that makes use of Becke-Style density functional theory [21] with various correlation functionals (LYP, P86 and PW91) [22]. The double- ζ basis set adds two sizes of orbital functions on heavy atoms and hydrogens, respectively, as well as diffuse functions on both.

The ground state geometries were obtained in the gas phase by full geometry optimization, starting from structural data. Solvent effects are

relevant in MPA stability, since polarity differences can induce significant changes in their relative energies in solution. There are several different flavors of PCM (i.e. CPCM, SCI-PCM); but we decided to use of PCM/B3LYP calculations to analyze the solvent effects on MPA complex. PCM calculations can be performed using HF, DFT as well as MP2 methods with diffuse functions without any problems for single point calculations. The PCM model is strongly basis set dependent [23]. It is important to stress that the PCM model does not consider the presence of explicit solvent molecules; hence specific solute-solvent interactions are not described and the calculated solvation effects arise only from mutual solute-solvent electrostatic polarization. The PCM cavity is defined by using Pauling [24] radius for each solute atom.

The standard A and B basis sets were used in all calculations. Literature analysis [25] shows that the geometries and relative stabilities of the structures calculated at B3LYP/6-31+G(d,p) level are in a good accord with experimental data. Pople et al., have shown that the absolute deviations for the bond lengths and angles are smaller than corresponding values obtained at such levels of theory as MP2/6-31G(d) and QCISD/6-31G(d). The earlier studies of

hydrogen binding in nucleic acid bases indicate that the B3LYP method yields reliable interaction energies that correspond to the MP2/6-31G(d,p) level data. Therefore, the B3LYP and B3PW91 methods were applied in all calculations reported in this paper.

RESULTS AND DISCUSSIONS

Theoretical results of the calculated hydrogen-bond geometries for structure of MPA complex in different solvents are given in Table 1 and the equilibrium structure obtained in the B3LYP/(H,O):6-31+G**+(Mo,P):LANL2DZ is shown in Figure 2.

Clearly, all structural parameters have undertaken many variations but we considered those of importance in the MPA complex. The data presented in Table 1 show that polar solvents increase the stability of MPA complex in compare to gas phase. The Energy of MPA Complex (1:1) in Different Solvents calculated by the DFT methods for B3LYP/A, B and B3PW91/ A, B are closer than the values obtained by the other methods. According to the previous studies, HF-optimized structures show essentially bigger deviations in hydrogen-bond lengths. The two series of basis sets of DFT techniques show similar trends in reproducing the hydrogen-bond angles.

Table 1. Energy of MPA Complex (1:1) in Different Solvents / (J/mol)

Solvent	ϵ	10^{-9} Energy of MPA Complex (1:1) / (J/mol)			
		B3LYP/A ^a	B3PW91/A	B3LYP/B ^b	B3PW91/B
DichloroEthane	10.36	-1.58299	-1.58257	-1.58273	-1.58228
THF	7.58	-1.58297	-1.58255	-1.58270	-1.58226
Chloroform	4.90	-1.58291	-1.58249	-1.58265	-1.58223
Benzene	2.25	-1.58276	-1.58234	-1.58249	-1.58205
Carbon Tetrachloride	2.23	-1.58276	-1.58234	-1.58249	-1.58205
Heptane	1.92	-1.58273	-1.58228	-1.58247	-1.58202

^aA: (H,O):D95**+(Mo,P):LANL2DZ

^bB: (H,O):6-31+G**+(Mo,P):LANL2DZ

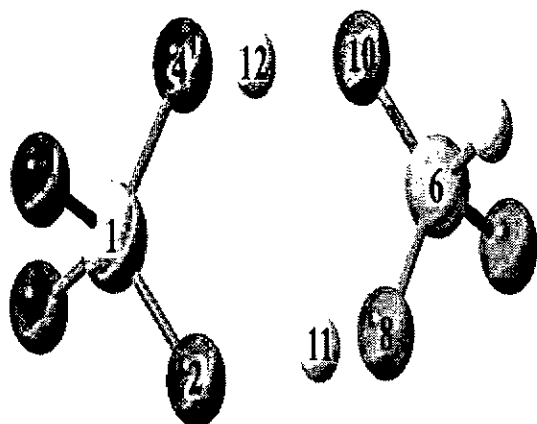


Fig. 2. Equilibrium structure of MPA complex in the B3LYP/(H, O): 6-31+G**+(Mo, P): LANL2DZ.

As shown in the table 1, regarding to calculations, all methods & basis sets implied DichloroEthane, could makes the MPA complex has the most stable state; while Heptane makes the MPA complex has the most unstable state.

We plotted the MPA complex stability energy versus to $1/\epsilon$ Figure 2). The following equation is derived, It is necessary to mention based on Correlation coefficient this equation is trustable ($R^2=0.9949$). J/mol is considered as the unit of energy.

$$E = 639064.27(1/\epsilon) + 1.58305 \times 10^9$$

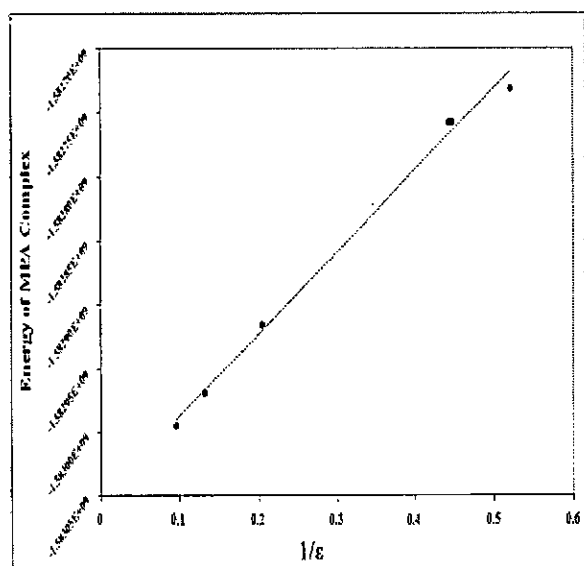


Fig. 3. Linear dependence of MPA Energy to $1/\epsilon$ for solvents.

Tables 2 to 4 are shown that the longest hydrogen bonds correspond to O...H bonds present in MPA complex, while small deviations of hydrogen-bond angles from 180° manifest themselves in the complex of MPA, with increase of polarity solvent. Interestingly, MPA complex, which according to the calculations are strongly bound species among the hydrogen-bonded systems have also the shortest hydrogen bonds and almost straight hydrogen-bond angles. The shorter hydrogen bonds and the straight hydrogen-bond angles do not necessarily reflect stronger binding. On the contrary, significantly high calculated interaction energies, display two O...H hydrogen bonds and the deviation from 180° in the corresponding O-H...O angles.

The geometrical analysis of hydrogen bonds in the calculated assemblies gives useful insights into internal cooperative effects regarding the complex stabilities but at the same time provides no general rules for any qualitative or semi-quantitative conclusions concerning the relative stabilities of the complex. On the other hand the hydrogen-bond geometry data could be profitable for the critical evaluation of particular level of theory by the calculated molecular parameters.

According to results that are shown in Table 1, the MPA complex in different solvents has minimum energy configuration with similar interaction energies for most polar solvents.

Analogues of results that have been shown in Tables 1 to 4 indicates that the interaction energies and geometrical data that have been calculated by two methods for B3LYP/ A, B and B3PW91/ A, B are similar values. Therefore, calculations of the counterpoise correction are strongly dependent upon molecular structure. Also, in this investigation the configuration calculated by these DFT methods, with increase polarity of used solvents has shown more stability for all Methods.

Table 2. The Lengths of Hydrogen Bonds:
B3LYP & B3PW91/ (H,O): D95**+(Mo, P): LANL2DZ

Solvent	ϵ	Bond Length / (Å) - (B3LYP)				Bond Length / (Å) - (B3PW91)			
		O (2) ... H (11)	O (8) ... H (11)	O (4) ... H (12)	O (10) ... H (12)	O (2) ... H (11)	O (8) ... H (11)	O (4) ... H (12)	O (10) ... H (12)
DichloroEthane	10.36	1.660	0.990	1.070	1.380	1.631	1.000	1.080	1.360
THF	7.58	1.660	0.990	1.070	1.380	1.631	1.000	1.080	1.360
Chloroform	4.90	1.660	0.990	1.060	1.410	1.625	1.000	1.070	1.370
Benzenc	2.25	1.687	0.990	1.040	1.460	1.656	0.990	1.050	1.420
Carbon Tetrachloride	2.23	1.690	0.990	1.040	1.460	1.659	0.990	1.050	1.420
Heptane	1.92	1.701	0.990	1.040	1.460	1.667	0.990	1.040	1.440

Table 3. The Lengths of Hydrogen Bonds:
B3LYP & B3PW91/ (H,O): 6-31+G(d,p)+(Mo, P): LANL2DZ

Solvent	ϵ	Bond Length / (Å) - (B3LYP)				Bond Length / (Å) - (B3PW91)			
		O (2) ... H (11)	O (8) ... H (11)	O (4) ... H (12)	O (10) ... H (12)	O (2) ... H (11)	O (8) ... H (11)	O (4) ... H (12)	O (10) ... H (12)
DichloroEthane	10.36	1.723	0.990	1.030	1.480	1.689	0.990	1.050	1.430
THF	7.58	1.723	0.990	1.030	1.480	1.689	0.990	1.050	1.430
Chloroform	4.90	1.730	0.990	1.030	1.490	1.695	0.990	1.040	1.440
Benzene	2.25	1.762	0.990	1.020	1.520	1.723	0.990	1.030	1.480
Carbon Tetrachloride	2.23	1.761	0.990	1.020	1.530	1.722	0.990	1.030	1.480
Heptane	1.92	1.786	0.980	1.020	1.520	1.736	0.990	1.030	1.500

Table 4. Bond Angles of Hydrogen Bonds: B3LYP & B3PW91/ A&B

Solvent	ϵ	Bond Angle (Deg) - (B3LYP/A)		Bond Angle (Deg) - (B3PW91/A)		Bond Angle (Deg) - (B3LYP/B)		Bond Angle (Deg) - (B3PW91/B)	
		O (2) H (11) O (8)	O (2) H (11) O (8)	O (2) H (11) O (8)	O (4) H (12) O (10)	O (2) H (11) O (8)	O (4) H (12) O (10)	O (2) H (11) O (8)	O (4) H (12) O (10)
DichloroEthane	10.36	176.9	176.9	177.0	178.2	177.3	179.4	177.7	179.2
THF	7.58	176.9	176.9	177.0	178.2	177.3	179.3	177.7	179.2
Chloroform	4.90	177.8	177.8	177.0	178.2	177.0	179.6	177.3	179.1
Benzene	2.25	176.7	176.7	177.0	178.2	176.6	179.7	176.9	179.6
Carbon Tetrachloride	2.23	176.6	176.6	176.8	178.0	176.4	179.7	176.7	179.8
Heptane	1.92	176.6	176.6	176.8	177.7	176.4	179.6	176.8	179.5

A: (H, O): D95**+(Mo, P): LANL2DZ

B: (H, O): 6-31 +G(d,p)+(Mo, P): LANL2DZ

CONCLUSTIN

Our theoretical studies indicate that the stability information of a single complex in different polarity of solvents could not be directly used to obtain stability data for hydrogen-bonded assemblies in general. It is noteworthy that the geometrical analysis of the hydrogen bonds may present useful insights into their cooperative effects affecting the complex stabilities. Two conclusions are drawn from this study: (1) the major difficulty with ab initio calculations of hydrogen-bonded interactions at the theoretical levels in solvent phase explored herein lies with inadequate basis set; and (2) systems with more than 3 or 4 heavy atoms (Mo, P, O, ...) are, at present, too expensive to treat accurately both hardware and software reasons.

Salvation effects are therefore important in such systems as they are in the hydrogen bond complexes. The present study shows that the results obtained by the DFT methods for B3LYP/A & B and B3PW91/ A & B are similar trends.

The MPA complex has minimum energy configuration with similar binding energies, but very different polarity values of solvent for A and B basis sets are significant. When polarity values are increased for, the binding energies of these systems are remarkably insensitive to basis set and its effect for stability of MPA complex is very

important. The calculated results showed the solvents with higher dielectric constants strengthen the intermolecular hydrogen bonding interaction between Molybdate and Phosphonic Acid, although some of the solvents affected on stability due to the relaxation of the solute geometry under the influence of the solvent such as Benzene and Heptane.

According to the results of this research, using DFT level for optimization of geometry in solvent phase, the best results of energetic and geometry for this group of complexes were obtained by B3LYP/(H₂O):6-31+G**+(Mo,P):LANL2DZ calculations.

The calculated results showed the strength of the intermolecular interaction between the MPA complex and solvent played an important role in the system stability. It is well observed that energy values increase linearly with decrease in dielectric constants.

Finally, we come to this conclusion that the growing performance of ab initio methods most probably offers certain advantages in the rational design of new materials in the future.

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