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The Solvent Effects on Relative Stability of Molybdate-Phosphonic Acid Complex: A Theoretical Study

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ABSTRACT

The structure and relative stability of Molybdate-Phosphonic Acid (MPA) Complex in different solvents have been carried out using Density Functional Theory (DFT) methods. 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. 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 Beeke3LYP calculations.

Keywords: Molybdate: Phosphonic Acid, Solvent Effect: DFT

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, 3] and Mó [4-6] as well as other authors [7] 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 [8]. When solvent effects are taken in to account, the reverse order is found, in accordance with the experimental data [9].

DFT methods, particularly hybrid functional methods have evolved to a powerful quantum chemical tool for a determination of the electronic structure of molecules. In the framework of DFT approach, different exchange and correlation functionals are routinely used [10]. 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 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. Earlier ab initio studies of the structures and stabilities of hydrogen-bonded assemblies of nucleic acid basis carried out [11-15] and showed that quantum chemical techniques could now be used to

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perform calculations on molecular systems of practical significance.

METHODS

All DFT calculations were carried out with the Gaussian 03 program [19]. 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 [20] with various correlation functionals (LYP, P86 and PW91) [21]. The double-ζ basis set adds two sizes of orbital functions on heavy atoms and hydrogens, respectively, as well as diffuse functions on both.

Solvent effects are relevant in MPA stability since polarity differences can induce significant changes in their relative energies in solution. We decided to use of PCM/B3LYP calculations to analyze the solvent effects on MPA complex. 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 [16].

The standard A and B basis sets were used in all calculations. Literature analysis [17, 22] 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) [23]. 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 [12]. 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 1.

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 [25]. 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 / (a.u.)

Solvent	ε	Energy of MPA Complex (1:1) / (a.u)			
		B3LYP/ A[a]	**B3PW91/A**	**B3LYP/ B**[b]	**B3PW91/B**
Water	78.39	-602.98	-602.81	-602.88	-602.71
DMSO	46.70	-602.95	-602.79	-602.85	-602.68
NitroMethane	38.20	-602.95	-602.95	-602.55	-602.85
Ethanol	24.55	-602.97	-602.81	-602.87	-602.70
Acetone	20.70	-602.95	-602.79	-602.85	-602.68

[a] **A:** (H,O)-D95**+ (Mo,P):LANL2DZ

[b] **B:** (H,O).6-31+G**+(Mo,P):LANL2DZ

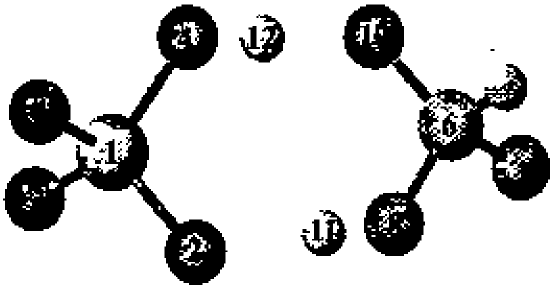

Fig.1. Equilibrium structure of MPA complex in the B3LYP/(H, O): 6-31+G**+(Mo, P): LANL2DZ.

The differences between the total energies of H-bonding with electron transfer do not show a regular trend when changing from gas phase to most polar solvents (water).

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 hydragen-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 [26].

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 (water).

Analogues of results that have been shown in Tables 1 to 4 indicates that the interaction energies and geometricals 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. Bond Lengths and Band Angles of H-Banding of MPA Complex (1.1) in Gas Phase Based on Different DFT Methods in A & B Basis Sets

Method/Bassis Set	Bond Length / (Å)				Bond Angle / (Deg)	
	O (2)...H (11)	O (8) - H (11)	O (4)...H (12)	O (10)...H (12)	O (2) H (11) O (8)	O (4) H (12) O (10)
B3LYP/A	1.779	0.993	1.025	1.554	175.0	178.1
B3LYP/B	1.885	0.986	1.014	1.628	175.6	179.5
B3PW91/A	1.747	0.994	1.030	1.525	175.1	178.0
B3PW91/B	1.844	0.987	1.019	1.587	175.7	179.7

A: (H, O) D95**+(Mo P): LANL2DZ
B: (H, O): 6-31+G(d,p)+(Mo, P): LANL2DZ

Table 3. Bond Lengths of H-Bonding of MPA Complex (1.1) in Different Solvents Based on B3LYP & B3PW91/(H, O): D95**+(Mn, P): LANL2DZ Calculations

Solvent	ln 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)
Water	4.36	1.624	1.000	1.050	1.410	1.594	1.000	1.070	1.370
DMSO	3.84	1.659	0.990	1.070	1.380	1.621	1.000	1.100	1.320
NitroMethane	3.64	1.660	0.990	1.070	1.380	1.662	0.490	1.070	1.380
Ethanol	3.20	1.627	1.000	1.050	1.410	1.608	1.000	1.060	1.390
Acetone	3.03	1.670	0.990	1.078	1.380	1.637	1.000	1.080	1.360

Table 4 Bond Lengths of H-Bonding of MPA Complex (1.1) in Different Solvents Based on B3LYP & B3PW91/(H, O): 6-31+G(d,p)+(Mo, P): LANL2DZ Calculations

Solvent	ln 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)
Water	4.36	1.675	0.990	1.030	1.480	1.655	0.990	1.040	1.450
DMSO	3.84	1.719	0.990	1.040	1.470	1.689	0.990	1.050	1.420
NitroMethane	3.64	1.718	0.990	1.040	1.470	1.720	0.990	1.040	1.470
Ethanol	3.20	1.685	0.990	1.030	1.490	1.657	0.990	1.040	1.440
Acetone	3.03	1.730	0.990	1.030	1.480	1.692	0.990	1.050	1.430

CONCLUSION

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 majar 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 (Ma, P, O, ...) are, at present, too expensive to treat accurately both hardware and software reasons.

Solvation 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.

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

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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