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ABSTRACT

Water is expected to play a crucial role in modulating the conformational energetics of organophosphates (OP). It is expected that these different energetics may be important in controlling the interaction, lifetime and reaction kinetics of OP in solution and at interface of surfaces. Unfortunately, while there have been extensive *ab initio* simulations of OP in vacuum, there are a limited number of computational studies that either implicitly or explicitly incorporate water into the investigations. Simulations involving water would provide structural and dynamical details of the OP-water complexes, along with the impact of hydration on the observed energies. Initial computational investigations have proven either inclusive or inconsistent when evaluating different OP. For example, simulations incorporating polarized continuum models (PCM) show that the conformational potential energy surface (PES) of Sarin is essentially unchanged from the PES obtained from simulations in vacuum. In contrast, simulations of the PES for dimethyl methyl phosphonate (DMMP) reveal distinct differences between the vacuum and PCM results. Incorporation of the PCM produced changes in the energies of the different equilibrium conformers, with the relative energies of the higher energy conformers (III and IV) being reduced by approximately 2 kcal mol⁻¹, in comparison to the vacuum results. This observation would suggest that DMMP structural conformations originally dismissed based on the energetics from vacuum simulations, may become important in discussions involving the adsorption and kinetics of hydrated DMMP. The PCM results are also commonly at odds to results and trends obtained from *ab initio* calculations that explicitly included water molecules complexed to the OP. Presently it is unclear at what point increasing the number of explicit water converges to the PCM results. To investigate the impact of water on conformational energetics, we report a series of microhydration simulations. A large number of initial starting conformation were explored for the Sarin+nH₂O and DMMP+nH₂O complexes (n = 1, 2, 3), followed by optimization to a local equilibrium conformation. It is shown that these OP+Water complexes are very rich in structural conformations and exhibit a distribution of energies. We will present the implementation of an *ab initio* "Evolutionary Generation Tree" method to characterize these different microhydrated clusters and to map out transitions between energetically favorable conformers.

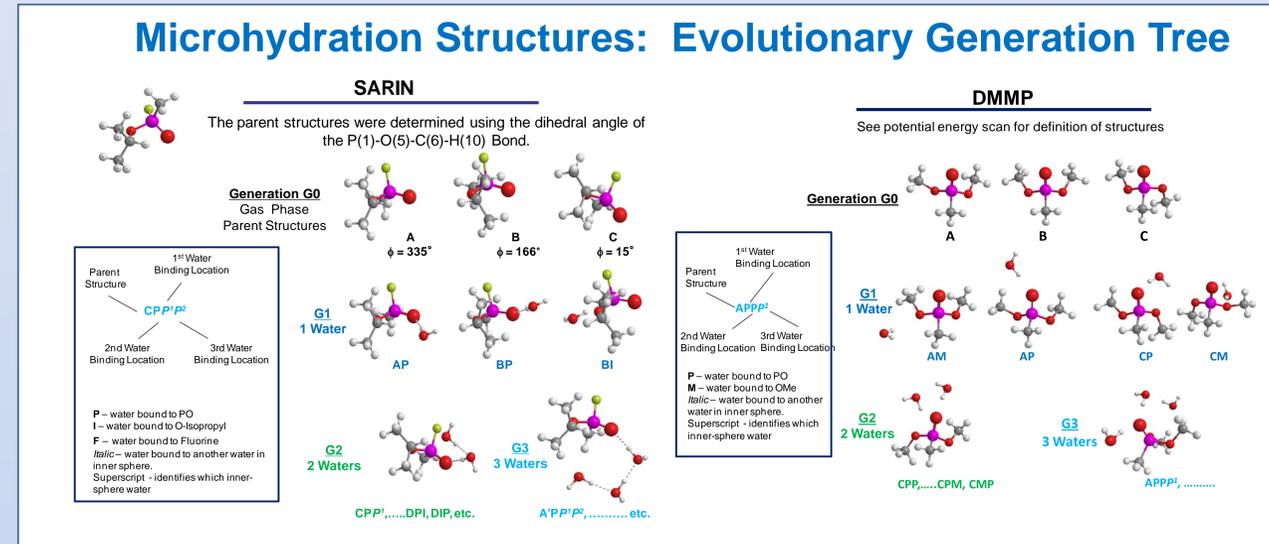


Table A: Relative predicted energies (kcal/mol) for gas phase conformers of DMMP optimized at B3LYP 6-311++G(2d,2p) in the gas phase.

Conformer	B3LYP	MP2	B3LYP (PCM)	MP2 (PCM)	ΔG_{rel} (B3LYP)	ΔG_{rel} (MP2)
A	0.0	0	0.0	0.0	-6.4	-6.3
B	0.2	0.3	0.5	0.5	-6.1	-6.1
C	2.3	2.0	0.5	0.2	-8.2	-8.0

Sarin

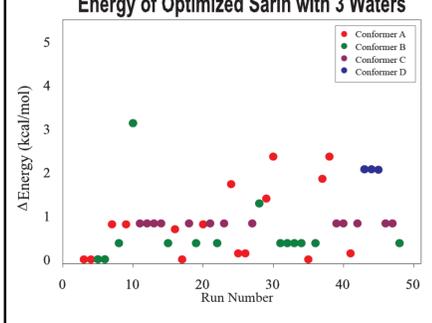
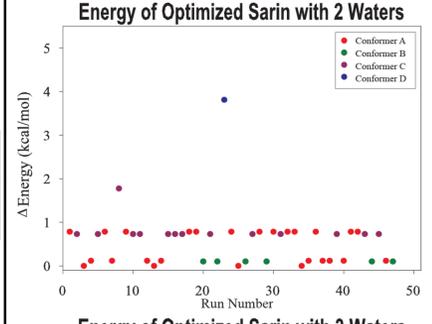
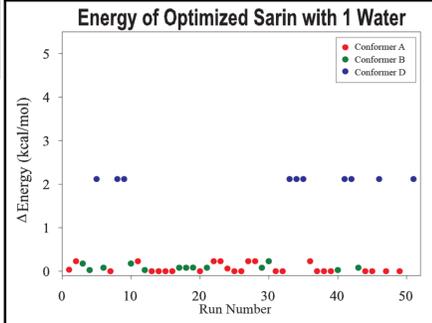


Table B: Energies of Water Dimer Complex

Energies	H ₂ O	2H ₂ O
E	-76.4620395 H	-152.93139931
E [†]	--	-152.93136855
BSSE	--	6.246x10 ⁻⁴ H (0.39 kcal mol ⁻¹)
E [†] (Opt)	--	-152.931376
$\delta^{formation}$	--	6.9x10 ⁻⁵ (0.043 kcal mol ⁻¹)
δ^{HB}	--	-7.36x10 ⁻² (4.62 kcal mol ⁻¹)
δ	--	-7.30x10 ⁻² (4.58 kcal mol ⁻¹)

E = Energies at DFT B3LYP/6-311++(2d,2p), E[†] = Corrected Energies for BSSE, $\delta^{formation}$ = deformation energy, δ^{HB} = hydrogen bonding energy.

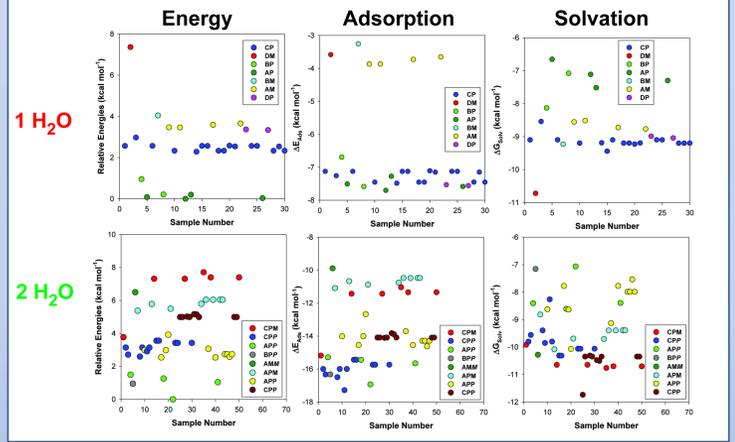
- The micro-hydration of Sarin shows only a small variation of $\Delta E(adsorption)$ with conformer.
- The addition of the 2nd and 3rd water to the hydration sphere produces a smaller change in the $\Delta E(adsorption)$.
- For 3 waters hydrated to Sarin the relative energies of the different conformation become intermingled.
- Hydrogen bonding between waters in the hydration sphere become the dominant energetic component with higher water content in comparison to the hydrogen bond to the P=O bond.
- There are subtle structural changes in the Sarin conformer with addition of explicit waters.

DMMP

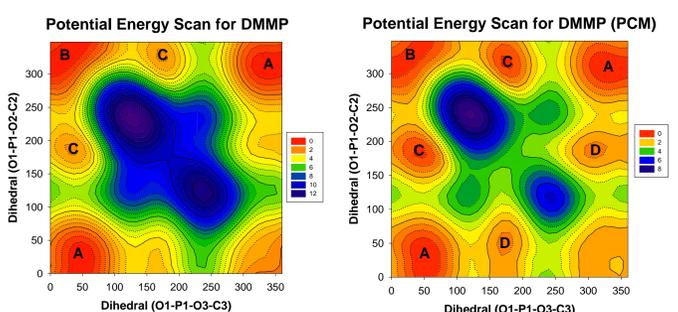
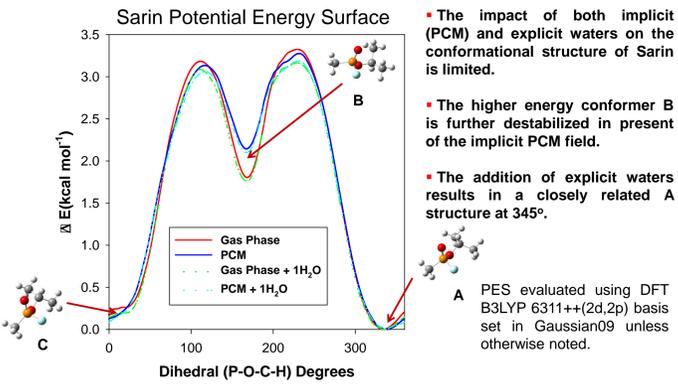
Table C: DMMP + 1H₂O, Micro-Solvation Energetics

Conformer	ΔE (kcal mol ⁻¹) ^a	ΔE_{ads} (kcal mol ⁻¹)	ΔE_{ads}^{opt} (kcal mol ⁻¹)	δ_{BSSE}^{opt} (kcal mol ⁻¹)	BSSE (kcal mol ⁻¹)	$\langle \Delta G_{rel} \rangle$ (kcal mol ⁻¹)
AP	0.00 [0.08 (0.09)]	-7.70 [-7.51 (0.18)]	-7.13 [-7.05 (0.09)]	0.44 [0.34 (0.09)]	0.48 [0.47 (0.02)]	-7.52 [-7.14 (0.37)]
AM	3.46 [3.55 (0.10)]	-3.87 [-3.78 (0.11)]	-3.67 [-3.59 (0.10)]	0.17 [0.16 (0.01)]	0.58 [0.57 (0.01)]	-8.77 [-8.64 (0.13)]
BP	0.21 [0.58 (0.52)] ^b	-7.58 [-7.14 (0.63)]	-7.16 [-6.79 (0.52)]	0.31 [0.25 (0.09)]	0.49 [0.47 (0.03)]	-8.12 [-7.60 (0.74)]
BM	4.04 [-()] ^c	-3.25 [-()] ^c	-3.32 [-()] ^c	-0.09 [-()] ^c	0.52 [-()] ^c	-9.22 [-()] ^c
CP	2.28 [2.48 (0.18)]	-7.48 [-7.29 (0.17)]	-7.11 [-6.92 (0.18)]	0.74 [0.27 (0.14)]	1.11 [0.49 (0.17)]	-9.44 [9.14 (0.18)]
CM	-- ^d	-- ^d	-- ^d	-- ^d	-- ^d	-- ^d
DP	3.34 [-()] ^e	-7.56 [-()] ^e	-- ^e	-- ^e	0.45 [-()] ^e	-8.99 [-()] ^e
DM	7.36 [-()] ^f	-3.58 [-()] ^f	-- ^f	-- ^f	0.64 [-()] ^f	-10.72 [-()] ^f

^a Relative energies with respect to lowest AP+1H₂O configuration. Values given are lowest (average (Std. Dev.)) based on analysis of 30 configurations. ^b Only 2 of this configuration observed. ^c Only a single example of this configuration observed. ^d No examples of this DMMP+1H₂O configuration observed. ^e No stable gas phase conformation.



Conformational Energetics in Gas Phase and PCM



CONCLUSIONS

- The addition of explicit waters in the hydration produces a rich variation in the energetics of both Sarin and DMMP.
- At higher hydration levels the presence of other conformers become energetically favorable.
- The structural perturbation are small for Sarin and DMMP.
- The adsorption energies for 2 explicit waters are on the order of the adsorption energy for SARIN and DMMP on SiOH surfaces. This suggest that micro-hydration of Sarin and DMMP will interfere with the SiO₂ surface adsorption.

This work a part of a larger coordinated effort that includes: T17-012, *Ab Initio Studies into the Role of Water on the Energetics of Organophosphate Surface Adsorption*, Janelle Jenkins (SNL), T14-009 *Molecular Simulations of Dimethyl Methylphosphonate Aqueous Solutions*, Pratt (Tulane University).

