Isomerization of $PO_3^-\cdot(H_2O)_n$ Clusters to $H_2PO_4^-\cdot(H_2O)_{n-1}$: Transition States and Barrier Heights

Buyong Ma, Yaoming Xie, Mingzuo Shen, Paul v. R. Schleyer, and Henry F. Schaefer, III*

Contribution from the Center for Computational Quantum Chemistry, The University of Georgia, Athens, Georgia 30602

Received May 10, 1993®

Abstract: Several mechanisms for the isomerization reactions of the $PO_3^-\cdot(H_2O)_n$ clusters (n = 1, 2, and 3) to $H_2PO_4^-\cdot(H_2O)_{n-1}$ have been studied using *ab initio* quantum mechanical methods, resulting in predictions of the transition state structures, isomerization barrier heights, exothermicities, and products. Basis sets as large as triple-ζ plus double polarization plus f functions have been used with self-consistent-field, second-order perturbation theory, configuration interaction, and coupled cluster methods. The isomerization barrier ($\Delta G°$) for $PO_3^-\cdot H_2O$ to $H_2PO_4^-$ is 32 kcal mol^{-1} at the DZP+diff SCF level, 25 kcal mol^{-1} at the DZP CISD level, and 22 kcal mol^{-1} at the DZP+diff MP2 level. The isomerization barriers for $PO_3^-\cdot(H_2O)_2$ and $PO_3^-\cdot(H_2O)_3$ are lower by only a few kilocalories per mole than for $PO_3^-\cdot H_2O$ via four-centered transition states and lower by about 5 kcal mol^{-1} by six-center transition states. The PO_3^- anion is thermodynamically stable in the gas phse only when the PO_3^-:H_2O molar ratio is below 1:3. However, even with the 1:3 molar ratio, the $PO_3^-\cdot(H_2O)_3$ cluster is expected to be a product along with $H_2PO_4^-\cdot(H_2O)_2$. The $H_2PO_4^-$ anion forms double-donor double-acceptor hydrogen bonds with H_2O similar to those predicted earlier for PO_3^-. The C_2 symmetry conformation of $H_2PO_4^-$ is more stable than the C_s form, while the C_{2v} conformation is a stationary point with two imaginary vibrational frequencies. The potential energy surfaces for $H_2PO_4^-\cdot H_2O$ and $H_2PO_4^-\cdot(H_2O)_2$ are qualitatively similar to that for isolated $H_2PO_4^-$. The exothermicities ($-\Delta H°$) of the reactions $PO_3^-\cdot(H_2O)_n \rightarrow H_2PO_4^-\cdot(H_2O)_{n-1}$ are 18 (n = 1), 22 (n = 2), and 21 kcal mol^{-1} (n = 3) at the DZP+diff SCF level of theory. The DZP+diff SCF hydration exothermicity of $H_2PO_4^-$ (i.e. $-\Delta H°$ for $H_2PO_4^- + H_2O \rightarrow H_2PO_4^-\cdot H_2O$) is 14 kcal mol^{-1}, while that for $H_2PO_4^-\cdot H_2O$ is 8 kcal mol^{-1}. The analogous hydration exothermicities for the isomers $PO_3^-\cdot H_2O$ and $PO_3^-\cdot(H_2O)_2$ are 11 and 10 kcal mol^{-1}, respectively. Although much progress has been made, several questions remain concerning the relationships between the present theoretical results and existing experiments.

1. Introduction

Phosphates are among the most important compounds in living systems, as phosphorylation is a key to biochemical synthesis. The mechanisms of the chemical reactions that involve the formation and destruction of phosphate esters are vital to the understanding of living systems.[1] One of the major possibilities requires that the coordination number of phosphorus decrease from four to three, to produce a "metaphosphate" that then adds a nucleophile to yield product.

$$ROPO_3H^- \rightarrow ROH + [PO_3^-] \qquad (1)$$

$$[PO_3^-] + H_2O \rightarrow H_2PO_4^- \qquad (2)$$

Extensive research has focused on this mechanism,[2a,3] and there is considerable debate over whether PO_3^- can exist as a free entity in water. However, due to the high reactivity of the PO_3^- anion, some positive but mostly negative results have been obtained, depending on the nature of the solvent systems. There appears to be no evidence that requires the formation of a metaphosphate monoion in aqueous solution.[2a] However, very recently, it has been reported[4] that while discrete PO_3^- is an intermediate in the hydrolysis of monothiopyrophosphate (MTP), it is too reactive and cannot escape from its solvation sphere; PO_3^- is captured by water or another nucleophile that competes with water in solvating MTP.

Despite its high reactivity in aqueous solution, the clusters of the PO_3^- anion with water molecules are believed to be stable in the gas phase.[5,6] In the gas phase the pertinent reactions seem to be

$$PO_3^- + nH_2O \rightarrow PO_3^-\cdot(H_2O)_n \qquad (3)$$

$$PO_3^-\cdot(H_2O)_n \rightarrow H_2PO_4^-\cdot(H_2O)_{n-1} \qquad (4)$$

Our previous research[7] has attempted to characterize the intermediate $PO_3^-\cdot(H_2O)_n$ clusters and essential agreement with the experimental data has been obtained. Nevertheless, there are still many unresolved questions. For example, how does isomerization from $PO_3^-\cdot(H_2O)_n$ to $H_2PO_4^-\cdot(H_2O)_{n-1}$ occur? Why is the behavior of PO_3^- in the gas phase and in aqueous solution so different? The heart of the present research is to understand the isomerization reactions, which are difficult to investigate experimentally. In order to relate gas-phase and solution-phase chemistry, we need to know the barrier heights for the isomerizations. To our knowledge, there is no published theoretical research on the $PO_3^-\cdot(H_2O)_n$ isomerization barriers, which would provide the key to understanding the thermodynamics in the gas phase.[8,13]

® Abstract published in *Advance ACS Abstracts,* November 1, 1993.

[1] Westheimer, F. H. *Chem. Rev.* **1981**, *81*, 313. Westheimer, F. H. *Science* **1987**, *235*, 1173.

[2] (a) Herschlag, D.; Jencks, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 7579. Herschlag, D.; Jencks, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 7587. Herschlag, D.; Jencks, W. P. *J. Am. Chem. Soc.* **1990**, *112*, 1951. (b) Jencks, W. P. Personal communication.

[3] (a) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161. (b) Ramirez, F.; Marecek, J.; Minore, J.; Srivastava, S.; leNoble, W. *J. Am. Chem. Soc.* **1986**, *108*, 348. (c) Burgess, J.; Blundell, N.; Cullis, P. M.; Hubbard, C. D.; Misra, R. *J. Am. Chem. Soc.* **1988**, *110*, 7900. (d) Freeman, S.; Friedman, J. M.; Knowles, D. *J. Am. Chem. Soc.* **1987**, *109*, 3166. (e) Cullis, P. M.; Nicholls, D. *J. Chem. Soc., Chem. Commun.* **1987**, 783.

[4] Lightcap, E. S.; Frey, P. A. *J. Am. Chem. Soc.* **1992**, *114*, 9750.

[5] Henchman, M. J.; Viggiano, A. A.; Paulson, J. F.; Freedman, A.; Wormhoadt, J. *J. Am. Chem. Soc.* **1985**, *107*, 1453.

[6] Keesee, R. G.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 9015.

[7] Ma, B.; Xie, Y.; Shen, M.; Schaefer, H. F. *J. Am. Chem. Soc.* **1993**, *115*, 1943.

[8] Westheimer, F. H. Personal communication.

0002-7863/93/1515-11169$04.00/0

Only one of the possible isomerization products, $H_2PO_4^-$, has received theoretical attention previously. Kollman[9] has done pioneering research on the systematic conformational analysis of H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-} using quantum mechanical methods. Later, Ewig[10] studied phosphinic, phosphonic, and phosphoric acids. O'Keeffe[11] also examined similar systems extensively, including H_3PO_4 and $H_2PO_4^-$. In order to understand reaction 4, the structure and energetics of the $H_2PO_4^-{\cdot}(H_2O)_{n-1}$ clusters are as important as those for $PO_3^-{\cdot}(H_2O)_n$.

$H_2PO_4^-{\cdot}(H_2O)_{n-1}$ clusters and their formation are also important in biochemistry. For example, it is thought[12] that the difference in the solvation energies of the reactants and the products in the reaction

$$ATP + H_2O \rightarrow ADP + H_2PO_4^- \qquad (5)$$

contributes significantly to the ΔH and ΔG values.

Unlike the clustering reaction

$$PO_3^- + H_2O \rightarrow PO_3^-{\cdot}H_2O \qquad (6a)$$

there is no direct experimental measurement of the energy for the isomerization reaction

$$PO_3^-{\cdot}H_2O \rightarrow H_2PO_4^- \qquad (6b)$$

The values deduced from indirect experiments differ from one another blatantly[13]—the ΔH° for isomerization 6b derived from Unkel and Freedman's experiments[13a] is about −58 kcal mol^{-1} but that derived from Rudnyi's experiments[13b] is only about −24 kcal mol^{-1}. The latter value is generally considered to be more reasonable.[13]

In addition to reactions 6a and 6b, two other isomerization reactions

$$PO_3^-{\cdot}(H_2O)_2 \rightarrow H_2PO_4^-{\cdot}H_2O \qquad (7a)$$

$$PO_3^-{\cdot}(H_2O)_3 \rightarrow H_2PO_4^-{\cdot}(H_2O)_2 \qquad (8a)$$

are important. Experiments by Keesee and Castleman[6] have shown that ΔH° for the related process

$$PO_3^-{\cdot}(D_2O)_2 + D_2O \rightarrow D_2PO_4^-{\cdot}(D_2O)_2 \qquad (8b)$$

is −16.3 kcal mol^{-1}. However, our previous work[7] showed that for the clustering reaction

$$PO_3^-{\cdot}(D_2O)_2 + D_2O \rightarrow PO_3^-{\cdot}(D_2O)_3 \qquad (8c)$$

the theoretical ΔH° is −9.7 kcal mol^{-1} at the DZP+diff SCF level. If both experiment and theory were correct, then the deuterated isomerization reaction 8a would be exothermic by only 6.6 kcal mol^{-1}. This would be 17.4 kcal mol^{-1} below the lower experimental value[13] for reaction 6b, which involves only one water molecule. A difference of this magnitude due to the appendage of two water molecules seems surprising. Thus, reliable theoretical evaluations of the gas-phase exothermicities of these isomerization reactions are desirable.

There are two kinds of products, $PO_3^-{\cdot}(H_2O)_n$ and $H_2PO_4^-{\cdot}(H_2O)_{n-1}$, for the reactions of the PO_3^- anion with water molecules. In order to avoid confusion, we use the terms "clustering reaction" and "hydration reaction" for the formation of $PO_3^-{\cdot}(H_2O)_n$ and $H_2PO_4^-{\cdot}(H_2O)_n$, respectively, even though other workers use the term "hydration" to refer to the formation of $PO_3^-{\cdot}(H_2O)_n$ clusters in the literature.

2. Theoretical Methods

The basis sets adopted here include double-ζ plus polarization (DZP)[14,15] and DZP plus diffuse functions (DZP+diff) for the P and O atoms[16] and are the same as those used in our previous work on the equilibrium geometries of $PO_3^-{\cdot}(H_2O)_n$ clusters.[7] In order to test possible basis set effects, a very large basis set, TZ2P with f function for heavy atoms, was employed as well. For the TZ2P+f basis set, two sets of five pure spherical d functions and one set of seven pure spherical f functions are used for heavy atoms, with the orbital exponents being

$$\alpha_d(P) = 1.2, 0.3, \alpha_f(P) = 0.45; \qquad \alpha_d(O) = 1.7, 0.425, \alpha_f(O) = 1.4$$

For the hydrogen atom, two sets of p functions and one set of five pure spherical d functions are used in the TZ2P+f basis, with the orbital exponents being $\alpha_p(H) = 1.5, 0.375$, $\alpha_d(H) = 1.0$.

The Hartree–Fock or self-consistent-field (SCF) approach has been used to locate stationary points for several conformations via analytic first derivative techniques. Subsequently, analytic energy second derivative techniques are used to determine vibrational frequencies. Finally, the configuration interaction method with single and double excitations (CISD)[17] and the coupled cluster method including single and double excitations (CCSD)[18] are used independently to optimize the geometries. For the CISD and CCSD methods, only the valence electrons were explicitly correlated. Thus the core-like (phosphorus 1s, 2s and 2p; oxygen 1s) SCF molecular orbitals were constrained to be doubly occupied in all configurations. Also the corresponding core-like virtual orbitals were excluded from the CISD and CCSD procedures. With the DZP basis set, the number of basis functions for $H_2PO_4^-$, $H_2PO_4^-{\cdot}H_2O$, and $H_2PO_4^-{\cdot}(H_2O)_2$ are 93, 118, and 143, respectively. The DZP CISD wave functions for $H_2PO_4^-$ (C_2 symmetry) included 223 729 configurations. With the DZP+diff basis set, the CISD wave functions for the $H_2PO_4^-$ anion include 400 689 configurations. The computations were carried out using the program PSI developed in this research group.[19a] The program TURBOMOLE[19b] was used to locate the transition states for the isomerizations of $PO_3^-{\cdot}(H_2O)_2$ and $PO_3^-{\cdot}(H_2O)_3$ and to evaluate single-point energies at the second-order Møller–Plesset perturbation[20] (MP2) level of theory. For the MP2 calculations no core electrons were frozen and geometries were taken from the DZP SCF and DZP+diff SCF optimizations.

The exothermicities for the formation of the $H_2PO_4^-{\cdot}(H_2O)_n$ clusters, i.e., isomerization energies, are defined as follows:

$$n = 0: \quad \Delta E_e = E[PO_3^-{\cdot}H_2O] - E[H_2PO_4^-]$$

$$n = 1: \quad \Delta E_e = E[PO_3^-{\cdot}(H_2O)_2] - E[H_2PO_4^-{\cdot}H_2O]$$

$$n = 2: \quad \Delta E_e = E[PO_3^-{\cdot}(H_2O)_3] - E[H_2PO_4^-{\cdot}(H_2O)_2]$$

The zero-point corrected energy differences (ΔE_0) are based on the zero-point vibrational energies evaluated within the harmonic approximation using the DZP SCF and DZP+diff SCF methods.

For the energetic comparisons with experimental data, the enthalpy changes are evaluated as follows:[21]

---

(9) (a) Hayes, D. M.; Kollman, P. A.; Rothenberg, S. *J. Am. Chem. Soc.* **1977**, *99*, 2150. (b) Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier Scientific Publishing Co.: New York, 1974; p 90.

(10) Ewig, C. S.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 1965.

(11) O'Keeffe, M.; Domenges, B.; Gibbs, G. V. *J. Phys. Chem.* **1985**, *89*, 2304.

(12) (a) Voet, D.; Voet, J. G. *Biochemistry*; John Wiley & Sons: New York, 1990; p 411. (b) Ewig, C. S.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1988**, *110*, 79.

(13) Henchman, M. J. Personal communication and references cited: (a) Unkel, W.; Freedman, A. *AIAA J.* **1983**, *21*, 1648. (b) Rudnyi, E. B.; Vovk, O. M.; Sidorov, L. N.; Sorokin, I. D.; Alikhanyen, A. S. *High Temp. (Engl. Transl.)* **1986**, *24*, 56.

(14) (a) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. (b) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823. (c) Dunning, T. H.; Hay, P. J. In *Mordern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3, p 1.

(15) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F. *J. Chem. Phys.* **1989**, *89*, 7382.

(16) (a) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comp. Chem.* **1983**, *4*, 294. (b) Spitznagel, G. W.; Clark, T.; Schleyer, P. v. R. *J. Comp. Chem.* **1987**, *8*, 1109.

(17) (a) Brooks, B. R.; Laidig, W. D.; Saxe, P.; Goddard, J. D.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1980**, *72*, 4652. (b) Rice, J. E.; Amos, R. D.; Handy, N. C.; Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *85*, 963.

(18) (a) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. (b) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F. *J. Chem. Phys.* **1989**, *89*, 7382.

(19) (a) Yamaguchi, Y.; Frisch, M. J.; Gaw, J. F.; Schaefer, H. F.; Binkley, J. S. *J. Chem. Phys.* **1986**, *84*, 2262. (b) Ahlrichs, R.; Bar, M.; Häser, M.; Horn, H. *Chem. Phys. Lett.* **1989**, *162*, 165.

(20) (a) Møller, C.; Plesset, M. S. *Phys. Res.* **1934**, *46*, 618. (b) Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quantum Chem. Symp.* **1977**, *11*, 49. (c) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem. Symp.* **1978**, *14*, 91. (d) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(21) Del Bene, J. E.; Mettee, H. D.; Frisch, M. J.; Luke, B. T.; Pople, J. A. *J. Phys. Chem.* **1983**, *87*, 3279.

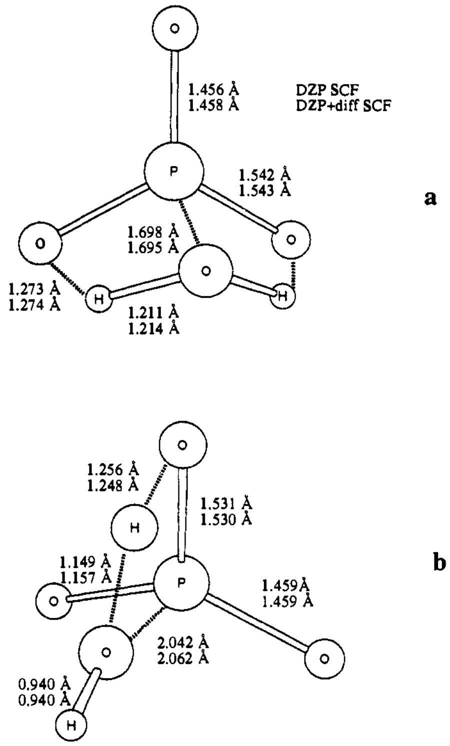


Figure 1. Two C_s symmetry stationary points (each with two imaginary vibrational frequencies) related to the isomerization of $PO_3^-\cdot H_2O$ to $H_2PO_4^-$.

$$\Delta H^\circ = \Delta E_e + \Delta E_v{}^\circ + \Delta(\Delta E_v)^{298} + \Delta E_r{}^{298} + \Delta E_t{}^{298} + \Delta(PV)$$

where $\Delta E_v{}^\circ$ is the difference between the zero-point vibrational energies of reactants and product at 0 K, and $\Delta(\Delta E_v)^{298}$ is the change in the vibrational energy difference in going from 0 to 298 K. The final terms account for changes in the number of rotational and translational degrees of freedom and the work term.

Entropy changes (ΔS°) have been evaluated from standard statistical mechanical relationships,[22] and free-energy changes (ΔG°) are evaluated from the standard relationship $\Delta G = \Delta H - T\Delta S$. In all such considerations the vibrational frequencies evaluated at the DZP SCF and DZP+diff SCF levels are used. The standard state is 1 atm at 298 K.

Basis set superposition errors (BSSE) were not examined in this research. Generally, BSSE may be important when dealing with bond energies of 5 kcal mol^{-1} or less, where the BSSE effect can be larger than the energetic quantity of interest.[23] However, the anionic hydrogen bonds under investigation here are significantly stronger. Also, the diffuse functions introduced into the basis set reduce the importance of BSSE.[23] Moreover, this view is reinforced by the good agreement (omitting BSSE corrections) with the experimental thermochemistry for the $PO_3^-\cdot(H_2O)_n$ systems.[7]

3. Results and Discussion

A. The Transition States and Barriers for the Isomerizations of $PO_3^-\cdot(H_2O)_n$ to $H_2PO_4^-\cdot(H_2O)_{n-1}$. I. Isomerization Mechanisms. The stability of the PO_3^- anion in the gas phase was first shown by Henchman,[5] who observed no reaction with the H_2O molecule. Keesee and Castleman have reported[6] that the gas-phase product of the PO_3^- anion and the H_2O molecule is the $PO_3^-\cdot H_2O$ cluster. The isomerization of $PO_3^-\cdot H_2O$ to $H_2PO_4^-$ is a prototypical reaction for understanding PO_3^- chemistry.

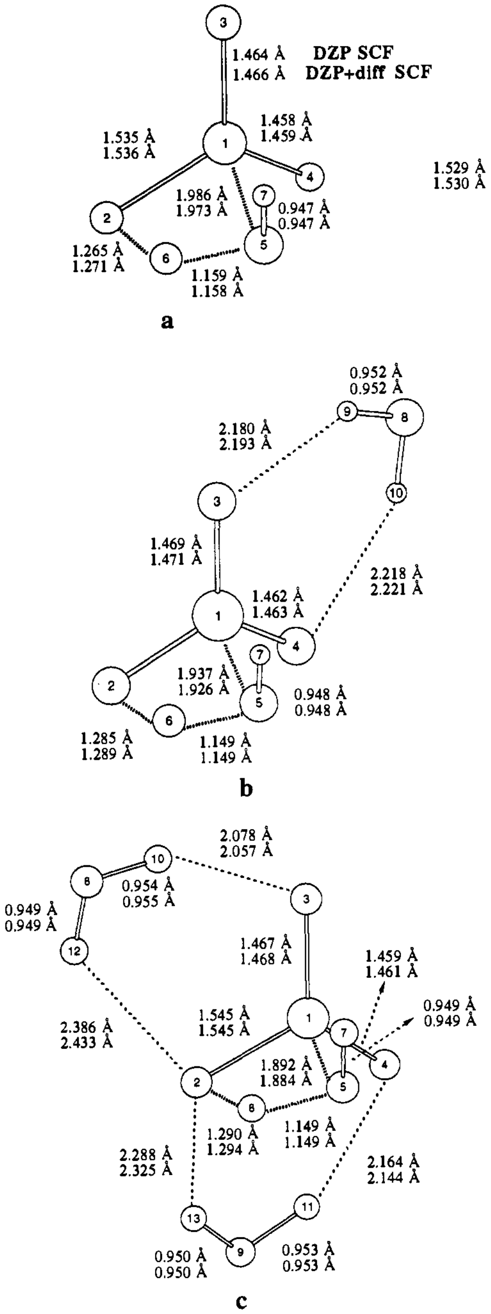


Figure 2. The four-center transition states from $PO_3^-\cdot(H_2O)_n$ to $H_2PO_4^-\cdot(H_2O)_{n-1}$: (a) $PO_3^-\cdot H_2O$ to $H_2PO_4^-$; (b) $PO_3^-\cdot(H_2O)_2$ to $H_2PO_4^-\cdot H_2O$; (c) $PO_3^-\cdot(H_2O)_3$ to $H_2PO_4^-\cdot(H_2O)_2$.

Starting from the C_{2v} symmetry structure of $PO_3^-\cdot H_2O$ (the global minimum in Figure 2 of ref 7), there are several possible mechanisms for isomerization. In the first, the H_2O moiety directly transfers two hydrogen atoms to PO_3^- and forms one additional P–O bond (Figure 1a). The barrier for this mechanism, with two O–H bonds to be broken, implies a radical intermediate species[2b] and is too high in energy to afford a realistic pathway. The corresponding stationary point has two imaginary vibrational frequencies, and thus it is not a true transition state. The second possible mechanism posits that the planes of the H_2O moiety and PO_3^- anion are perpendicular to one another. However, the corresponding stationary point also has two imaginary vibrational frequencies (Figure 1b) and therefore is not a transition state.

The favored mechanism for $PO_3^-\cdot H_2O$ isomerization requires that the planes of PO_3^- and H_2O moieties are almost parallel to one another, and one hydrogen atom is transferred from the H_2O to the PO_3^- anion. The resulting transition structure is depicted in Figure 2a. This mechanism is easy to understand; one of the lone pairs of H_2O points to the C_3 axis of PO_3^- and can be stabilized by the positive charge at the phosphorus atom. At the transition state, the bond length (DZP+diff SCF) for the original O–H bond (0.945 Å) is stretched to 1.158 Å, the length of the newly formed PO–H bond is about 1.271 Å, and the new P–O bond length is 1.973 Å.

---

[22] Hout, R. F., Jr.; Levi, B. A.; Hehre, W. J. *J. Comp. Chem.* **1982**, *3*, 234.

[23] See, for example: Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104 and references therein.

Table I. Harmonic Vibrational Frequencies (cm^{-1}) for the Transition State for the Reaction $PO_3^-\cdot(H_2O)_2 \rightarrow H_2PO_4^-\cdot H_2O$ at the DZP SCF Level of Theory

four-centered structure (Figure 2b)		six-centered structure (Figure 3a)	
DZP[a]	mode	DZP[a]	mode
4169 (3035)	stre O_5–H_7	4188 (3048)	stre O_8–H_{10}
4135 (3027)	stre O_8–H_{10}	4152 (3026)	stre O_5–H_7
4079 (2944)	stre O_8–H_9	2300 (1700)	stre O_5–H_6
2160 (1555)	bend P–O_5–H_6	1821 (1314)	trigonal def
1849 (1356)	bend H_9–O_8–H_{10}	1784 (1285)	bend H_7–O_6–H_6
1532 (1111)	tors P–O_2–H_6–O_5	1553 (1123)	pucking
1415 (1411)	stre P–O_4	1451 (1452)	stre P–O_4
1317 (1307)	stre P–O_2	1423 (1082)	asym def
1070 (769)	stre P–O_2	1300 (1296)	stre P–O_3
876 (680)	bend H_7–O_5–P	1054 (991)	bend P–$O_2\cdots H_6$
775 (507)	bend H_6–O_5–P	952 (779)	bend O_4–P–O_3
726 (511)	tors H_9–O_8–H_{10}–O_4	804 (728)	stre $O_2\cdots H_9$
625 (507)	tors H_6–O_5–P–O_2	691 (536)	bend H_6–O_8–H_{10}
602 (620)	out–of–plane O_3–P	607 (593)	out–of–plane O_3–P
520 (512)	bend O_3–P–O_2	571 (526)	O–P–O rocking
477 (522)	bend O_4–P–O_2	542 (487)	stre $O_8\cdots H_6$
408 (295)	tors P–O_4–H_{10}–O_8	510 (456)	stre $O_8\cdots H_6$
394 (282)	bend O_4–H_{10}–O_8	481 (418)	out–of–plane H_7–O_5
324 (314)	bend O_5–P–O_2	438 (334)	bend H_6–O_8–H_{10}
261 (246)	bend O_5–P–O_4	405 (393)	stre O_5–H_6
161 (54)	stre $O_3\cdots H_9$	313 (298)	stre $O_2\cdots H_9$
77 (75)	stre $O_3\cdots H_9$	295 (273)	O–P–O twisting
37 (36)	tors O_3–P_1–O_4–H_{10}	44 (43)	asym torsion
1707*i* (1254*i*)	stre O_5–H_6, stre $O_2\cdots H_9$	1276*i* (953*i*)	stre $O_8\cdots H_9$, stre $O_2\cdots H_9$

[a] The results in parentheses refer to the deuterated transition state, i.e., that for $PO_3^-\cdot(D_2O)_2 \rightarrow D_2PO_4^-\cdot D_2O$.

Can PO_3^- act as both an electrophile and an anion, as suggested by Loew and MacArthur?[24a] Our previous study of the $PO_3^-\cdot H_2O$ cluster[7] showed that there is no stationary point corresponding to an electrophilic role for PO_3^-. Thus a careful examination of the transition state is essential, with special attention to the nature of the reaction coordinate. If the reaction coordinate involves attack by the H_2O oxygen atom on the phosphorus atom in PO_3^-, then PO_3^- acts as an electrophile with regard to isomerization. On the other hand, if the hydrogen atom in H_2O attacks the oxygen atom in PO_3^-, then isomerization is still a "charge controlled" process and PO_3^- cannot be an electrophile. The reaction coordinate involves the transfer of a hydrogen atom from H_2O to PO_3^-, as indicated by the vibrational frequency analysis for the $PO_3^-\cdot H_2O \rightarrow H_2PO_4^-$ transition state. Thus PO_3^- reacts as a nucleophile rather than as an electrophile (or both) in the gas phase. However, it might be an electrophile in solution phase,[24b] where its negative charge could be less repulsive due to the presence of counterions.

We have considered two types of mechanisms for the two- and three-water isomerization reactions 7a and 8a. The first is rather simple, i.e., the solvation of the transition state for reaction 6b. As the number of water molecule increases, from $PO_3^-\cdot H_2O$ to $PO_3^-\cdot(H_2O)_2$ and $PO_3^-\cdot(H_2O)_3$, we suppose that each additional water molecule does not change the isomerization mechanism. Instead, hydrogen bonds form with the transition state for reaction 6b, as illustrated in Figure 2, parts b and c. This mechanism was confirmed by our vibrational frequency analysis (Table I). The Figure 2b structure is a saddle point corresponding to the isomerization from $PO_3^-\cdot(H_2O)_2$ to $H_2PO_4^-\cdot H_2O$. The nature of the reaction coordinate is the same as that for reaction 6b. Proceeding from the same principle, the transition state (Figure 2c) of reaction 8a was located by adding two more water molecules to form hydrogen bonds with the transition structure for reaction 6b.

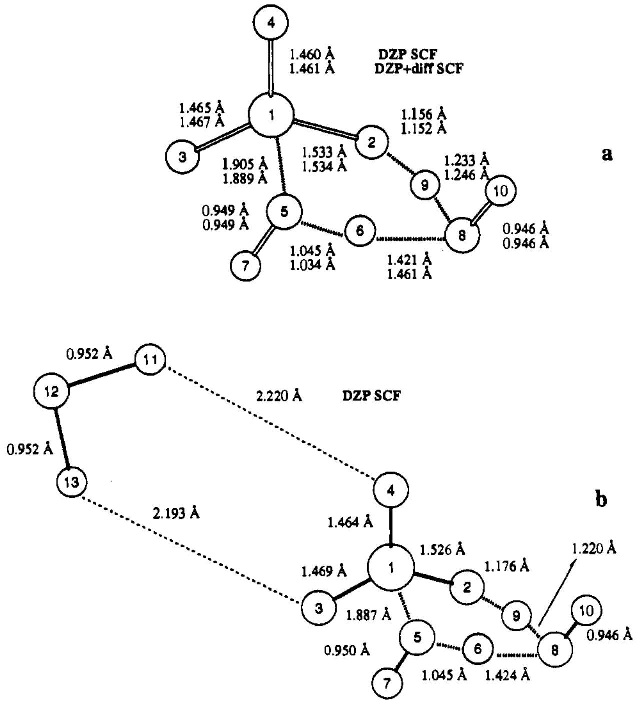


Figure 3. The six-center transition states from $PO_3^-\cdot(H_2O)_n$ to $H_2PO_4^-\cdot(H_2O)_{n-1}$: (a) $PO_3^-\cdot(H_2O)_2$ to $H_2PO_4^-\cdot H_2O$, (b) $PO_3^-\cdot(H_2O)_3$ to $H_2PO_4^-\cdot(H_2O)_2$.

For the second possible mechanism of reaction 7a, we considered a six-center instead of four-center transition state,[25] consisting of a water dimer interacting with PO_3^-. Evleth[26] was the first to locate such a six-center transition structure, his study being done at the 6-31G* SCF level. Starting from Evleth's geometries, we located a DZP+diff SCF transition state, which has a shorter new P–O bond length (1.889 Å) than that in Evleth's structure (1.926 Å) (Figure 3a). Due to the decrease of electrostatic repulsion in the six-center arrangement, the barrier height for the six-center transition structure is lower than that of the four-centered structure. Nevertheless, there are other factors that must be taken into consideration to compare the four- and six-centered mechanism properly:

(a) The six-center transition state, even with a lower barrier, may not be feasible in an ion–molecule reaction[6] in which the

---

[24] (a) Loew, L. M.; MacArthur, W. R. *J. Am. Chem. Soc.* **1971**, *99*, 1019. (b) Friedman, J. M.; Freeman, S.; Knowles, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3166.

[25] (a) Heidrich, D.; van Eikema Hommes, N. J. R.; Schleyer, P. v. R. *J. Comp. Chem.*, submitted for publication. (b) Lambert, C.; Hampel, F.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1209.

[26] Evleth, E. M. Personal communication.

Table II. Barrier Heights (Four-Center Mechanism) for the Isomerization of $PO_3^-\cdot(H_2O)_n$ to $H_2PO_4^-\cdot(H_2O)_{n-1}$

	$n = 1$[a,b]					$n = 2$[a,c]					$n = 3$[a,c]				
theoretical levels	$\Delta E_e^\ddagger$	$\Delta E_0^\ddagger$	$\Delta H^{\circ\ddagger}$	$-\Delta S^{\circ\ddagger}$	$\Delta G^{\circ\ddagger}$	$\Delta E_e^\ddagger$	$\Delta E_0^\ddagger$	$\Delta H^{\circ\ddagger}$	$-\Delta S^{\circ\ddagger}$	$\Delta G^{\circ\ddagger}$	$\Delta E_e^\ddagger$	$\Delta E_0^\ddagger$	$\Delta H^{\circ\ddagger}$	$-\Delta S^{\circ\ddagger}$	$\Delta G^{\circ\ddagger}$
DZP SCF	30.8	28.8	27.7	8.8	30.3	29.2	27.5	26.3	10.2	29.3	28.0	26.5	24.6	15.1	29.1
		(29.6)	(28.5)	(9.5)	(31.3)	**25.1**	**22.9**	**20.9**	**16.7**	**25.9**	**22.0**				
DZP+diff SCF	32.2	30.2	29.1	9.3	31.9	30.4	28.8	27.6	10.9	30.8	29.2	27.9	26.5	10.2	29.5
		(31.1)	(29.9)	(10.0)	(32.9)	**26.2**	**24.2**	**22.3**		**25.1**					
DZP CISD	25.6	23.6	22.5		25.1										
DZP MP2	21.6	19.6	18.5		21.1	20.1	18.4	17.2		20.3	18.5	17.0	15.1		19.6
						13.9	**11.7**	**9.7**		**14.7**					
DZP+diff MP2	22.4	20.4	19.3		22.1	21.3	19.7	18.5		21.8	19.2	17.8	16.4		19.4
						14.7	**12.7**	**10.8**		**16.1**					

[a] The values of ΔH and ΔG are in kcal mol^{-1}, and ΔS is in cal/(K·mol). The standard state is 1 atm at 298 K. [b] The values in parentheses refer to the deuterated species, i.e., the barrier heights for $PO_3^-\cdot(D_2O)_n \rightarrow D_2OP_4^-\cdot(D_2O)_{n-1}$. [c] The values in boldface refer to the six-center mechanism.

collision complex has a short lifetime.[26] Three-body collisions in general occur infrequently. Therefore, experiments are expected to give a final judgment concerning the true mechanism. If the transition state were detectable, it would be easy to tell whether the four- or six-center transition structure is involved. There are distinguishable IR differences between the two kinds of structures. As indicated in Table I, the four-center structure has three vibrational modes (OH stretch) above 4000 cm^{-1} (3600 cm^{-1}, if scaled by 0.9); the six-center structure has only two, with the third vibrational frequency dropped to about 2200 cm^{-1} due to its two-proton transfer nature.

(b) For the six-center transition state itself, a significant degree of charge transfer has occurred from the PO_3^- to the waters, the OH semianions (Figure 3) having a net charge of about −0.6. According to Evleth[26] the SCF method may not be satisfactory for this kind of transition structure, and he suggests that the MP2 method will not repair the situation.

(c) Fortunately, even though the six-center transition state has the lower barrier, it does not qualitatively affect our conclusions based on the four-center transition state. We report the barriers for both mechanisms for comparative purposes.

II. Reactivity of PO_3^- with Water Molecules. The $PO_3^-\cdot(H_2O)_n$ isomerization barriers can be discussed in terms of the potential-energy or free-energy surfaces. If one were concerned with the motion of individual molecules over the barrier, the factor determining whether free and spontaneous motion will occur would be the potential energy.[27] However, we wish to understand some PO_3^- chemistry and to compare our theoretical predictions with the experimental results (high-pressure mass spectrometry).[6] Thus we are concerned with an assembly of molecules in a statistical distribution among energy states. Whether or not there is spontaneous reaction is determined by the free energy.[27] Thus we will primarily use the free energy surface in discussing the different reaction barriers.

For reaction 6b, $PO_3^-\cdot H_2O \rightarrow H_2PO_4^-$, the isomerization barrier (Table II) is $\Delta G^{\circ\ddagger} = 30.3$ kcal mol^{-1} at the DZP SCF level and $\Delta G^{\circ\ddagger} = 31.9$ kcal mol^{-1} at the DZP+diff SCF level. Consistent with hydrogen transfer from H_2O to PO_3^-, the barrier increases by about 1 kcal mol^{-1} for the isomerization of $PO_3^-\cdot D_2O$ due to the deuterium isotope effect. It is often observed that the Hartree–Fock (HF) method overestimates reaction barriers.[28] For reaction 6b, the isomerization barrier ($\Delta G^{\circ\ddagger}$) decreases to 25.1 kcal mol^{-1} at the DZP CISD level, 21.1 kcal mol^{-1} at the DZP MP2 level, and 22.1 kcal mol^{-1} at the DZP+diff MP2 level.

The key difference between the gas-phase chemistry and liquid-phase chemistry of $PO_3^-\cdot(H_2O)_n$ is obviously the increase of the number of associated water molecules (n). For some higher value of the hydration number, n, the process

$$PO_3^-\cdot(H_2O)_n + H_2O \rightarrow H_2PO_4^-\cdot(H_2O)_n$$

is expected[6,13] to become spontaneous. This would explain why PO_3^- reacts promptly to form $H_2PO_4^-$ in solution but not in the gas phase. Henchman has suggested[13] that the barrier will decrease with increasing hydration (n). If the free energy of the barrier lies below the energy of the reactants, the isomerization reaction will occur spontaneously.

How can the reactivity of PO_3^- with water molecules be understood? Consider the hydration reactions of PO_3^- with one, two, and three water molecules. The reactions forming the clusters $PO_3^-\cdot(H_2O)_n$ require no activation. The present discussion is based on the results at the DZP+diff MP2 level, at which the isomerization barriers (free energy $\Delta G^{\circ\ddagger}$) are significantly lower than those at the SCF level. The four-center transition states (Figure 2) are used in the present discussion, unless six-center structures are specified.

For $PO_3^-\cdot(H_2O)_2$ isomerization 7a, the barrier ($\Delta G^{\circ\ddagger}$) is 30.8 kcal mol^{-1} at the DZP+diff SCF level and 21.8 kcal mol^{-1} at the DZP+diff MP2 level. The isomerization barrier does decrease due to the second water, but is only 1.1 kcal mol^{-1} lower than that for $PO_3^-\cdot H_2O$ at the DZP+diff SCF level and 0.3 kcal mol^{-1} at the DZP+diff MP2 level. The barrier for the isomerization of $PO_3^-\cdot(H_2O)_3$ decreases in an analogous manner: $\Delta G^{\circ\ddagger} = 29.5$ kcal mol^{-1} at the DZP+diff SCF level and $\Delta G^{\circ\ddagger} = 19.4$ kcal mol^{-1} at the DZP+diff MP2 level. These barriers are still relatively large, even for the six-center mechanism ($\Delta G^{\circ\ddagger} = 16.1$ kcal mol^{-1} at the DZP MP2 level for the $PO_3^-\cdot(H_2O)_2$ isomerization).

There are two modes for the reaction of PO_3^- with one water molecule. PO_3^- could first form a stable cluster $PO_3^-\cdot H_2O$ with the water molecule (reaction 6a) and then isomerize to $H_2PO_4^-$ (reaction 6b). Alternatively, PO_3^- might react with a water molecule directly to form $H_2PO_4^-$ without formation of a stable cluster intermediate (reaction 6c).

$$PO_3^- + H_2O \rightarrow PO_3^-\cdot H_2O \tag{6a}$$

$$PO_3^-\cdot H_2O \rightarrow H_2PO_4^- \tag{6b}$$

isomerization barrier $\Delta G^{\circ\ddagger} = 22.1$ kcal mol^{-1}

$$PO_3^- + H_2O \rightarrow H_2PO_4^- \tag{6c}$$

isomerization-hydration barrier $\Delta G^{\circ\ddagger} = 17.4$ kcal mol^{-1}

Clearly, both reactions 6b and 6c are inhibited by the barriers involved (Tables II and III). When only one water molecule reacts with PO_3^-, the more possible product is the barrier-free $PO_3^-\cdot H_2O$, even though the $H_2PO_4^-$ species lies lower in energy (see Section C). This explains why PO_3^- is stable in the gas phase.

The reactions of PO_3^- involving two water molecules are more complex. Some possibilities are indicated by the following equations:

$$PO_3^-\cdot(H_2O)_2 \rightarrow H_2PO_4^-\cdot H_2O \tag{7a}$$

isomerization barrier $\Delta G^{\circ\ddagger} = 21.8$ kcal mol^{-1}

$$PO_3^-\cdot H_2O + H_2O \rightarrow PO_3^-\cdot(H_2O)_2 \tag{7b}$$

---

[27] Laidler, K. L. *Theories of Chemical Reaction Rates*; McGraw-Hill Book Co.: New York, 1969; p 76.

[28] Schaefer, H. F. *J. Phys. Chem.* **1985**, *89*, 5336.

Table III. Barrier Heights (Four-Center Mechanism) for the Reactions Forming $H_2PO_4^-{\cdot}(H_2O)_{n-1}$

	$\Delta H^{\circ\ddagger,b}$ kcal mol^{-1}				$\Delta G^{\circ\ddagger,b}$ kcal mol^{-1}				$\Delta S^{\circ\ddagger,b}$ kcal/(K·mol)	
	DZP		DZP+diff		DZP		DZP+diff			
	MP2[a]	SCF	MP2[a]	SCF	MP2[a]	SCF	MP2[a]	SCF	DZP	DZP+diff
reaction 6c	3.1	15.1	6.9	17.2	13.5	25.5	17.4	27.7	−35.0	−35.1
$PO_3^- + H_2O \rightarrow H_2PO_4^-$										
reaction 7d	−11.6	2.6	−11.9	5.1	7.5	21.7	7.1	25.2	−63.8	−63.7
$PO_3^- + 2H_2O \rightarrow H_2PO_4^-{\cdot}H_2O$	**−19.1**	**−2.8**	**−19.7**	**0.5**	**1.9**	**18.3**	**1.4**	**19.5**	**−70.3**	
reaction 7e	3.8	15.2	3.6	17.0	15.1	26.5	14.9	29.4	−37.6	−37.9
$PO_3^-{\cdot}H_2O + H_2O \rightarrow H_2PO_4^-{\cdot}H_2O$	**−3.7**	**9.8**	**−4.2**	**12.4**	**9.5**	**23.1**	**9.2**	**23.7**	**−44.0**	
reaction 7a	17.2	26.3	18.5	27.6	20.3	29.3	21.8	30.8	−10.2	−10.9
$PO_3^-{\cdot}(H_2O)_2 \rightarrow H_2PO_4^-{\cdot}H_2O$	**9.7**	**20.9**	**10.8**	**23.0**	**14.7**	**25.9**	**16.1**	**25.1**	**−16.7**	
reaction 8d	−25.7	−9.0	−24.7	−5.5	3.4	20	2.5	21.7	−97.5	−91.1
$PO_3^- + 3H_2O \rightarrow H_2PO{\cdot}(H_2O)_2$										
reaction 8e	−10.3	3.6	−9.3	6.4	10.9	24.5	10.2	25.9	−71.3	−65.3
$PO_3^-{\cdot}H_2O + 2H_2O \rightarrow H_2PO_4^-{\cdot}(H_2O)_2$										
reaction 8b	3.1	14.7	5.7	17.0	16.2	27.8	17.1	28.4	−43.9	−38.3
$PO_3^-{\cdot}(H_2O)_2 + H_2O \rightarrow H_2PO_4^-{\cdot}(H_2O)_2$										

[a] Based on single point calculations at the MP2 level; the geometries were optimized at the SCF level, and the vibrational frequencies were evaluated at the SCF level. The standard state is 1 atm at 298 K. [b] The values in boldface refer to the six-center mechanism.

$$PO_3^- + 2H_2O \rightarrow PO_3^-{\cdot}(H_2O)_2 \qquad (7c)$$

$$PO_3^- + 2H_2O \rightarrow H_2PO_4^-{\cdot}H_2O \qquad (7d)$$

$$\text{hydration barrier } \Delta G^{\circ\ddagger} = 7.1 \text{ kcal mol}^{-1}$$

$$PO_3^-{\cdot}H_2O + H_2O \rightarrow H_2PO_4^-{\cdot}H_2O \qquad (7e)$$

$$\text{barrier } \Delta G^{\circ\ddagger} = 14.9 \text{ kcal mol}^{-1}$$

An important question is whether $H_2PO_4^-{\cdot}H_2O$ will be formed, i.e., whether PO_3^- will be stable with respect to isomerization with two water molecules. Experimentally, only the clustering reaction to $PO_3^-{\cdot}(H_2O)_2$ is observed. This result seems secure—the experimental ΔH° value for reaction 7b is consistent with our theoretical ΔH° value.[7] However, an examination of plausible $H_2PO_4^-{\cdot}H_2O$ formation reactions 7a, 7d, and 7e is instructive. Reactions 7a and 7e are less feasible, due to the size of the barriers. While there is no barrier on the *potential-energy* surface (Table III) for reaction 7d, this process has not been observed experimentally.[6] These reactions are governed by the free-energy surface. Reaction 7d is prevented by the *free-energy* barrier. It is important to note that reaction 7d may be possible by the mechanism involving the six-center transition state ($\Delta G^{\circ\ddagger} = 1.4$ kcal mol^{-1}); however this process has not been observed experimentally.[6] This fact indicates that the six-centered transition structure is unlikely.

$PO_3^-{\cdot}(H_2O)_3$ and $H_2PO_4^-{\cdot}(H_2O)_2$ are possible products for the reactions of PO_3^- involving three water molecules. Is the $PO_3^-{\cdot}(H_2O)_3$ species stable [without isomerizing to $H_2PO_4^-{\cdot}(H_2O)_2$]? Will the $H_2PO_4^-{\cdot}(H_2O)_2$ be formed even though the $PO_3^-{\cdot}(H_2O)_3$ is stable? It is easy to answer the first question, because isomerization reaction 8a has a 19.4 kcal mol^{-1} barrier ($\Delta G^{\circ\ddagger}$) at the DZP+diff MP2 level. Thus the $PO_3^-{\cdot}(H_2O)_3$ species will be formed (no barrier for cluster formation) and will be kinetically stable. To answer the second question, first recall the experimental results.[6] The experimental ΔH° for the association of $PO_3^-{\cdot}(H_2O)_2$ with the third water molecule is notably larger in magnitude than the clustering reactions 6a and 7b.[6] Keesee and Castleman suggested quite plausibly that reaction 8b is observed. However, this reaction has a large barrier ($\Delta G^{\circ\ddagger} = 16.2$ kcal mol^{-1}). The best energetic pathway to $H_2PO_4^-{\cdot}(H_2O)_2$ should be via the improbable four-body reaction 8d or the three-body reaction 8e.

$$PO_3^-{\cdot}(H_2O)_3 \rightarrow H_2PO_4^-{\cdot}(H_2O)_2 \qquad (8a)$$

$$\text{isomerization barrier } \Delta G^{\circ\ddagger} = 19.4 \text{ kcal mol}^{-1}$$

$$PO_3^-{\cdot}(H_2O)_2 + H_2O \rightarrow H_2PO_4^-{\cdot}(H_2O)_2 \qquad (8b)$$

$$\text{barrier } \Delta G^{\circ\ddagger} = 17.1 \text{ kcal mol}^{-1}$$

$$PO_3^-{\cdot}(H_2O)_2 + H_2O \rightarrow PO_3^-{\cdot}(H_2O)_3 \qquad (8c)$$

$$PO_3^- + 3H_2O \rightarrow H_2PO_4^-{\cdot}(H_2O)_2 \qquad (8d)$$

$$\text{hydration barrier } \Delta G^{\circ\ddagger} = 2.5 \text{ kcal mol}^{-1}$$

$$PO_3^-{\cdot}H_2O + 2H_2O \rightarrow H_2PO_4^-{\cdot}(H_2O)_2 \qquad (8e)$$

$$\text{barrier } \Delta G^{\circ\ddagger} = 10.2 \text{ kcal mol}^{-1}$$

Reactions 8d and 8e have no barriers on the potential-energy surface. However, reaction 8e has a 10.2 kcal mol^{-1} barrier on the free-energy surface. Reaction 8d has only a 2.5 kcal mol^{-1} barrier on the free-energy surface and is more feasible. It is especially true when the six-center transition state is considered, which may have a higher probability with three water molecules than with two. The barrier for reaction 8d vanishes for the six-center mechanism. However, even though $H_2PO_4^-{\cdot}(H_2O)_2$ will be formed, the $PO_3^-{\cdot}(H_2O)_3$ is expected to be a major intermediate. We discuss this point further in Section C.

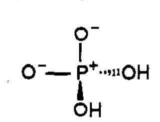
B. The Isolated Isomerization Products: $H_2PO_4^-{\cdot}(H_2O)_{n-1}$ (*n* = 1, 2, and 3). I. Structures and Energetics of $H_2PO_4^-{\cdot}(H_2O)_{n-1}$. The isomerization reactions of the $PO_3^-{\cdot}(H_2O)_n$ clusters are summarized by

$$PO_3^-{\cdot}(H_2O)_n \rightarrow H_2PO_4^-{\cdot}(H_2O)_{n-1} \qquad (4)$$

To augment our previous work on the $PO_3^-{\cdot}(H_2O)_n$ clusters[7] and the isomerization transition states discussed above, we have investigated the isomerization products $H_2PO_4^-$, $H_2PO_4^-{\cdot}H_2O$, and $H_2PO_4^-{\cdot}(H_2O)_2$. These species are very important in inorganic chemistry and in biochemistry.

Three conformations of $H_2PO_4^-$, with C_s, C_{2v}, and C_2 symmetries, are shown in Figure 4. The vibrational frequencies for the C_2 conformation are given in Table IV. The vibrational frequencies for the C_s conformation are rather similar to the latter and are not reported here.

Three are two kinds of P–O bonds in the $H_2PO_4^-$ species. The longer bonds (1.646 Å at the DZP+diff CISD level) are the P–OH single bonds. The shorter bonds (1.486 Å at the DZP+diff CISD level) may be represented as $P^+{-}O^-$ polar bonds.[29] This means the $H_2PO_4^-$ moiety is represented qualitatively by



Like the $H_2NO_4^-$ anion[28] and the closely related H_2SO_4 species,[31] the global minimum for the $H_2PO_4^-$ species has C_2 symmetry (top of Figure 4). A second minimum (middle of Figure

---

(29) Reed, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.

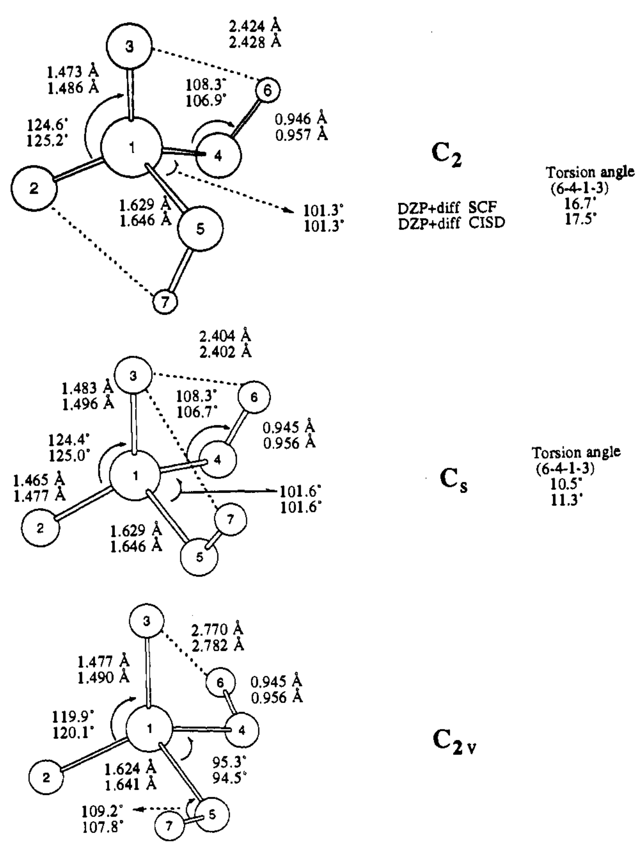


Figure 4. Three conformations of $H_2PO_4^-$ at the DZP+diff SCF and DZP+diff CISD theoretical levels.

Table IV. Harmonic Vibrational Frequencies (cm^{-1}) for the Global Minimum Structure (C_2 symmetry, top of Figure 4) of $H_2PO_4^-$ at the SCF level of Theory[a]

mode	symmetry	DZP	DZP+diff	TZ2P+f
sym O–H	A	4202 (3059)[a]	4199 (3057)[a]	4197 (3054)
asym O–H	B	4201 (3057)	4198 (3055)	4195 (3053)
asym P^+–O^-	B	1444 (1430)	1419 (1404)	1425 (1410)
sym P^+–O^-	A	1210 (1209)	1194 (1193)	1199 (1198)
bend P–O–H	B	1158 (930)	1151 (926)	1155 (921)
bend P–O–H	A	1137 (917)	1133 (911)	1137 (908)
asym P–OH	B	898 (876)	892 (867)	890 (875)
sym P–OH	A	870 (800)	865 (797)	867 (803)
bend HO–P^+–O^-	B	569 (563)	563 (558)	568 (562)
bend ^-O–P^+–O^-	A	566 (561)	558 (553)	563 (559)
bend HO–P^+–O^-	B	485 (446)	483 (445)	484 (446)
bend HO–P^+–O^-	A	427 (396)	424 (394)	426 (394)
bend ^-O–P^+–O^-	A	364 (360)	361 (357)	361 (356)
tors H–O–P^+–O^-	B	324 (239)	321 (237)	341 (251)
tors H–O–P^+–O^-	A	220 (165)	221 (166)	228 (173)

[a] The results in parentheses refer to the deuterated species $D_2PO_4^-$.

4) with C_s symmetry lies about 1 kcal mol^{-1} higher in energy. The C_{2v} symmetry $H_2PO_4^-$ stationary point (bottom of Figure 4) has two imaginary vibrational frequencies and is about 4 kcal mol^{-1} higher in energy than the C_2 conformation. The two imaginary vibrational frequencies correspond to the torsional movements of H–O–P^+–O^- going to the C_2 and the C_s symmetry conformations. These results are quite different from those of O'Keeffe et al.,[11] who assumed C_{2v} symmetry for $H_2PO_4^-$. Hayes, Kollman, and Rothenberg's[9a] earlier STO-3G SCF conformational results for $H_2PO_4^-$ are similar to ours—i.e., the C_{2v} symmetry structure is highest in energy while the C_s and C_2 structures are lower in energy—even though the geometries were not optimized in their research. The main difference between the C_{2v} conformation and the C_2 or C_s conformations is that the ^-O–P^+–O^- and HO–P–OH bond angles are smaller in the C_{2v} conformation.

Intramolecular hydrogen bonding is very important in the related $H_2NO_4^-$ system.[30] For $H_2PO_4^-$, due to the fact that the P–O bond is longer than the N–O bond, the intramolecular hydrogen bonds [2.428 Å (C_2) and 2.782 Å (C_{2v})] are expected to be weaker than those in H_2NO_4 and have more dipole–dipole character. The H–O–P^+–O^- torsional angle is about 11° (C_s) or 17° (C_2) in $H_2PO_4^-$, while the corresponding angles in the $H_2NO_4^-$ system are only 0° (C_s) or 5° (C_2), indicating a stronger intramolecular interaction. There is also an important "anomeric" effect,[32,33] namely the tendency for lone pairs to be *gauche* relative to polar bonds, operative in the $H_2PO_4^-$ conformational surface. The situation is similar for the isoelectronic H_2SO_4 system.[31]

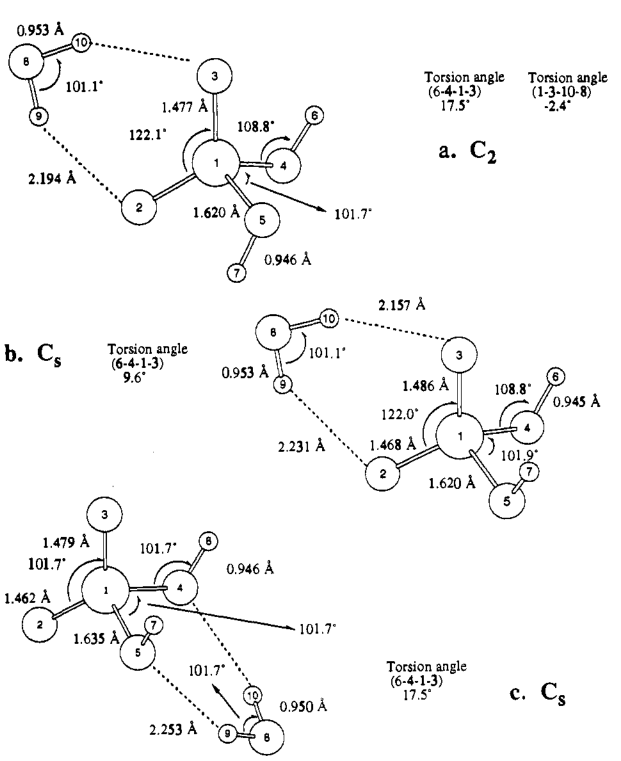


Figure 5. Three equilibrium geometries of $H_2PO_4^-\cdot H_2O$ at the DZP+diff SCF theoretical level.

The isomerization of $PO_3^-\cdot(H_2O)_2$ produces the $H_2PO_4^-\cdot H_2O$ anion, which also may be viewed as the solvation product of $H_2PO_4^-$ with H_2O. There are distinct orientations in which water can form intermolecular hydrogen bonds with the $H_2PO_4^-$ anion, i.e., to the different kinds of oxygen atoms in $H_2PO_4^-$. The H_2O molecule can form hydrogen bonds with the ^-O–P^+–O^- oxygens (Figure 5, parts a and b). The H_2O can also form hydrogen bonds with the HO–P–OH oxygen atoms (Figure 5c). Due to the higher negative charge on oxygen, the hydrogen bonding to the ^-O–P^+–O^- moiety is energetically favored by about 4 kcal mol^{-1}. We have considered C_2, C_s, and C_{2v} symmetries for the $H_2PO_4^-\cdot H_2O$ cluster. The potential energy surface for $H_2PO_4^-\cdot H_2O$ is similar to that for $H_2PO_4^-$; its global minimum also has C_2 symmetry, and the C_{2v} structure has two imaginary vibrational frequencies. The relative energy of the C_s conformation is 1 kcal mol^{-1}, and that of the C_{2v} conformation is 4 kcal mol^{-1} with respect to the C_2 symmetry structure. The vibrational frequencies for the C_2 $H_2PO_4^-\cdot H_2O$ are listed in Table V.

The last isomerization product we considered is $H_2PO_4^-\cdot(H_2O)_2$. For this cluster, the H_2O molecules form hydrogen bonds involving all four oxygen atoms of $H_2PO_4^-$. The global minimum also has C_2 symmetry (Figure 6a). The C_s conformation is 1 kcal mol^{-1} higher in energy (Figure 6b). Thus the conformation of $H_2PO_4^-$ determines the energy surface for the $H_2PO_4^-\cdot(H_2O)_n$ clusters, and solvation does not significantly change the relative energies.

---

(30) (a) Shen, M.; Xie, Y.; Schaefer, H. F.; Deakyne, C. A. *J. Chem. Phys.* **1990**, *93*, 3379. (b) Shen, M.; Xie, Y.; Schaefer, H. F.; Deakyne, C. A. *Chem. Phys.* **1991**, *151*, 187.

(31) Hofmann, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.*, to be published and references cited therein.

(32) Newton, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 256.

(33) Reed, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 7362. Reed, R. E.; Schleyer, P. v. R. *Inorg. Chem.* **1988**, *27*, 3969.

Table V. Harmonic Vibrational Frequencies (cm^{-1}) for the Global Minimum (Top of Figure 5) Structure of $H_2PO_4^-\cdot H_2O$ (C_2 Symmetry) at the SCF Level of Theory

mode	symmetry	DZP[a]	DZP+diff[a]	mode	symmetry	DZP[a]	DZP+diff[a]
stre PO–H	A	4202 (3059)	4198 (3056)	bend $^-$O–P$^+$–O$^-$	A	570 (567)	565 (561)
stre PO–H	B	4200 (3057)	4196 (3054)	bend HO–P$^+$–O$^-$	A	559 (517)	553 (508)
stre HO–H	B	4117 (3014)	4114 (3012)	bend P–O–H	A	488 (449)	486 (447)
stre HO–H	A	4066 (2934)	4061 (2932)	tors O–H···$^-$O–P$^+$	A	439 (390)	437 (390)
bend H_9–O_8–H_{10}	A	1856 (1401)	1834 (1384)	bend O–H···O$^-$	B	425 (365)	412 (363)
stre P$^+$–O$^-$	B	1417 (1358)	1399 (1341)	tors O–H···$^-$O–P$^+$	A	402 (304)	401 (297)
stre P$^+$–O$^-$	A	1209 (1208)	1197 (1196)	bend $^-$O–P$^+$–O$^-$	A	371 (299)	369 (296)
bend H–O–P	B	1150 (936)	1144 (932)	tors H–O–P$^+$–O$^-$	B	297 (219)	298 (220)
bend H–O–P	A	1132 (924)	1127 (919)	tors H–O–P$^+$–O$^-$	A	187 (161)	189 (156)
stre HO–P	B	926 (892)	917 (882)	stre H···O$^-$	A	166 (140)	161 (139)
stre HO–P	A	884 (802)	880 (799)	stre H···O$^-$	B	77 (75)	73 (71)
tors H–O–H···O$^-$	B	740 (580)	720 (570)	tors H···$^-$O–P$^+$–O$^-$	B	38 (37)	39 (38)

[a] The results in parentheses refer to the deuterated species $D_2PO_4^-\cdot D_2O$ cluster.

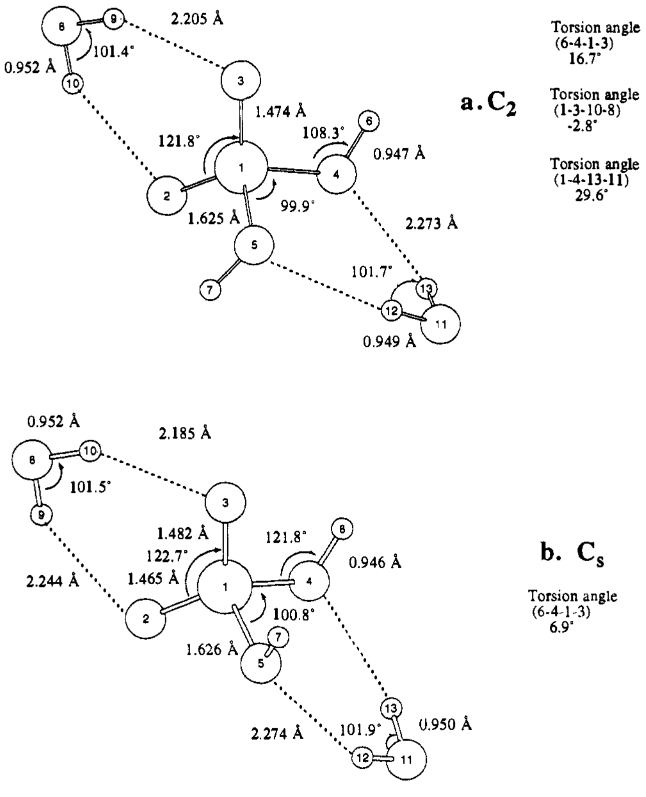


Figure 6. Two equilibrium geometries of $H_2PO_4^-\cdot(H_2O)_2$ at the DZP+diff SCF theoretical level.

The bond distance changes in the parent anion are a final interesting aspect of the hydration of $H_2PO_4^-$. The changes in distance of the two types of P–O bonds are related. When the H_2O molecule forms hydrogen bonds with $^-$O–P$^+$–O$^-$, the P$^+$–O$^-$ bonds are lengthened by 0.004 Å, but the P–OH single bonds are shortened by 0.009 Å (Figure 5). Hydrogen bonding of H_2O with HO–P–OH lengthens the P–OH single bonds by 0.006 Å but shortens the P$^+$–O$^-$ bonds by 0.004 Å. However, both the P$^+$–O$^-$ and the P–OH bond distances in $H_2PO_4^-\cdot(H_2O)_2$ are similar to those for the isolated $H_2PO_4^-$ anion. The two types of interactions in $H_2PO_4^-\cdot H_2O$ compensate one another. This may explain the significant difference between the theoretical and experimental structures[9b] of $H_2PO_4^-$. The theoretical bond distances (DZP+diff CISD) for the P$^+$–O$^-$ and P–OH bonds in isolated $H_2PO_4^-$ are 1.486 and 1.646 Å, respectively; the difference between bond distances is 0.16 Å. However, the experimental values[9b] are 1.50 and 1.55 Å, respectively, for the $H_2PO_4^-$ anion in the $KH_5(PO_4)_2$ crystal; the P$^+$–O$^-$ bonds are lengthened while the P–OH single bond is shortened, and thus the bond length difference is reduced significantly to 0.05 Å. A recent explanation attributed the large discrepancies between theoretical and experimental data to intermolecular forces in the crystal.[34] The countercation effect is important. The best position for the countercation on the $^-$O–P$^+$–O$^-$ side results in P$^+$–O$^-$ bond elongation and P–OH single-bond shortening. The stronger ion pair interaction (relative to hydrogen bonding) results in larger bond distance changes. Our studies of LiH_2PO_4 showing these countercation effects will be reported elsewhere; better agreement with experiment is achieved.

II. The Solvation of $H_2PO_4^-$. The clustering reaction of H_2O with $H_2PO_4^-$ has both similarities and differences with PO_3^-. The similarities are structural. The H_2O molecule forms double-donor double-acceptor hydrogen bonds with $H_2PO_4^-$, as was found[7] for PO_3^-. Both C_2 and C_s symmetry $H_2PO_4^-\cdot H_2O$ anions bind in this manner (Figure 5b).

The energy difference between PO_3^- and $H_2PO_4^-$ solvation reactions is significant (see the data in Table VI, corresponding to reactions 9 and 10).

$$H_2PO_4^- + H_2O \rightarrow H_2PO_4^-\cdot H_2O \qquad \Delta H^\circ = -13.5\ \text{kcal mol}^{-1} \quad (9)$$

$$H_2PO_4^-\cdot H_2O + H_2O \rightarrow H_2PO_4^-\cdot(H_2O)_2 \qquad \Delta H^\circ = -8.4\ \text{kcal mol}^{-1} \quad (10)$$

The $H_2PO_4^-$ species is about 3 kcal mol^{-1} more strongly solvated than either PO_3^- or $PO_3^-\cdot H_2O$ (Table VIII), due to the larger negative charge on the $^-$O–P$^+$–O$^-$ moiety in $H_2PO_4^-$. On the basis of their experimental results, Keesee and Castleman[6] also suggested that $H_2PO_4^-$ may be solvated more strongly than PO_3^-. The solvation energy for the $H_2PO_4^-\cdot H_2O$ anion ($\Delta H^\circ = -8.4$ kcal mol^{-1} for reaction 10) decreases sharply compared to $H_2PO_4^-$; $H_2PO_4^-\cdot H_2O$ is about 5 kcal mol^{-1} less strongly solvated than bare $H_2PO_4^-$, and even less than $PO_3^-\cdot H_2O$. The reason is that the second solvation site available is the HO–P–OH fragment, which has little negative charge. We have not predicted the solvation energy for $H_2PO_4^-\cdot(H_2O)_2$. However this solvation energy

$$H_2PO_4^-\cdot(H_2O)_2 + H_2O \rightarrow H_2PO_4^-\cdot(H_2O)_3 \quad (11)$$

is expected to be even less[6] than that for $H_2PO_4^-\cdot H_2O$, because no oxygen atoms in $H_2PO_4^-$ are as readily available as solvation sites for an additional (third) water molecule.[6] The experimental[16] ΔH° for reaction 11 is –12 kcal mol^{-1}, significantly higher than the value suggested by the present research (under –8 kcal mol^{-1}). Thus we suspect that the experimentally observed solvation reaction may be contaminated by the hydration reaction [$PO_3^-\cdot(H_2O)_3$ to $H_2PO_4^-\cdot(H_2O)_3$, reaction 12, next section]. We expand on this topic below.

C. The Exothermicity for the Isomerization of $PO_3^-\cdot(H_2O)_n$ and the Nature of the (2,3) Hydration Reaction. I. The Exothermicity for the Isomerization Reactions. Tables VII and VIII summarize our theoretical results pertaining to the energy

---

(34) Liang, C.; Ewig, C. S.; Stouch, T. R.; Hagler, A. T. *J. Am. Chem. Soc.* **1993**, *115*, 1537.

Table VI. Thermochemical Predictions for the Solvation of $H_2PO_4^-$ (kcal mol^{-1})[a]

	reaction 9 $H_2PO_4^- + H_2O \rightarrow H_2PO_4^-\cdot H_2O$					reaction 10 $H_2PO_4^-\cdot H_2O + H_2O \rightarrow H_2PO_4^-\cdot(H_2O)_2$				
theoretical levels	$-\Delta E_e$	$-E_0$	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$	$-\Delta E_e$	$-\Delta E_0$	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$
DZP SCF	16.0	13.6	14.1	5.6	28.4	10.3	8.5	8.8	0.7	27.0
		(14.2)	(14.5)	(5.9)	(29.0)		(8.7)	(8.9)	(0.7)	(27.4)
DZP+diff SCF	15.3	13.0	13.5	5.1	28.2	10.0	7.9	8.4	0.3	27.2
		(13.5)	(13.7)	(5.1)	(28.8)		(8.4)	(8.5)	(0.3)	(27.7)

[a] The values of ΔH and ΔG are in kcal mol^{-1}, and ΔS is in cal/(K·mol). The standard state is 1 atm at 298 K. The results in parentheses refer to fully deuerated species.

Table VII. Thermochemical Predictions for the Formation of $H_2PO_4^-$ (kcal mol^{-1})[a]

	reaction 6b $PO_3^-\cdot H_2O \rightarrow H_2PO_4^-$					reaction 6c $PO_3^- + H_2O \rightarrow H_2PO_4^-$				
theoretical levels	$-\Delta E_e$	$-\Delta E_0$	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$	$-\Delta E_e$	$-\Delta E_0$	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$
DZP SCF	19.1	18.3	19.1	16.5	8.6	33.6	30.4	31.7	21.3	34.8
		(18.1)	(18.9)	(16.3)	(8.5)			(31.9)	(21.4)	(35.2)
DZP+diff SCF	18.5	17.6	18.4	15.6	9.3	32.2	29.9	30.3	19.3	36.8
		(17.5)	(18.3)	(15.3)	(10)			(30.4)	(19.1)	(37.9)
TZ2P+f SCF						32.0	28.7	30.0	18.9	37.2
								(30.2)	(18.9)	(37.8)
TZ2P+f MP2						30.8	27.5	28.5	17.7	
DZP CISD	16.5	15.6	16.4			33.2	29.9	31.2		
DZP+diff CISD	16.6	15.7	17.6			32.2	29.0	30.3		
DZP CCSD	12.9	12.1	12.9			29.9	26.7	27.9		

[a] The values of ΔH and ΔG are in kcal mol^{-1}, and ΔS is in cal/(K·mol). The standard state is 1 atm at 298 K. The results in parentheses refer to fully deuterated species.

Table VIII. Thermochemical Predictions for the Formation of $PO_3^-\cdot(H_2O)_n$ and $H_2PO_4^-\cdot(H_2O)_{n-1}$ (kcal mol^{-1})[a]

	DZP SCF					DZP+diff SCF				
theoretical levels	$-\Delta E_e$	$-\Delta E_0$	$\Delta H°$	$-\Delta G°$	$-\Delta S°$	$-\Delta E_e$	$-\Delta E_0$	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$
reaction 7a	22.4	21.4	22.3	19.4	9.6	21.4	20.3	21.2	18.1	10.4
$PO_3^-\cdot(H_2O)_2 \rightarrow H_2PO_4^-\cdot H_2O$		(21.3)	(22.2)	(19.4)	(9.6)		(20.2)	(21.2)	(18.1)	(10.4)
reaction 7e	35.4	32.2	33.4	22.3	37.1	33.8	30.5	31.8	20.7	37.4
$PO_3^-\cdot H_2O + H_2O \rightarrow H_2PO_4^-\cdot H_2O$			(33.7)	(22.5)	(37.5)			(32.0)	(20.7)	(38.1)
reaction 8a	20.8	19.8	20.7	18.4	7.8	20.2	19.1	20.1	17.3	9.4
$PO_3^-\cdot(H_2O)_3 \rightarrow H_2PO_4^-\cdot(H_2O)_2$		(19.7)	(20.6)	(18.3)	(7.9)		(19.1)	(20.1)	(17.3)	(9.5)
reaction 8b	32.4	29.3	30.6	19.7	36.6	31.4	28.3	29.6	18.4	37.5
$PO_3^-\cdot(H_2O)_2 + H_2O \rightarrow H_2PO_4^-\cdot(H_2O)_2$			(30.8)	(19.8)	(37.0)			(29.8)	(18.5)	(38.1)
reaction 6a	14.5	12.1	12.6	4.8	26.2	13.7	11.4	11.9	4.2	25.8
$PO_3^- + H_2O \rightarrow PO_3^-\cdot H_2O$										
reaction 7b	13.0	10.7	11.1	2.9	27.5	12.4	10.2	10.6	2.5	27.0
$PO_3^-\cdot H_2O + H_2O \rightarrow PO_3^-\cdot(H_2O)_2$										
reaction 8c	11.6	9.6	9.9	1.3	28.8	11.2	9.2	9.5	1.1	28.1
$PO_3^-\cdot(H_2O)_2 + H_2O \rightarrow PO_3^-\cdot(H_2O)_3$										

[a] The values of ΔH and ΔG are in kcal mol^{-1}, and ΔS is in cal/(K·mol). The standard state is 1 atm at 298 K. The results in parentheses refer to fully deuterated species.

changes for the isomerization reactions and the exothermicities for the total hydration reactions. There are no directly measured experimental values for the exothermicities of the reactions

$$PO_3^-\cdot H_2O \rightarrow H_2PO_4^- \qquad (6b)$$

and

$$PO_3^-\cdot(H_2O)_2 \rightarrow H_2PO_4^-\cdot H_2O \qquad (7a)$$

The indirectly derived estimates differ with each other greatly.[13] For the reaction

$$PO_3^- + H_2O \rightarrow PO_3^-\cdot H_2O \qquad (6a)$$

$\Delta H°$ derived from Unkel and Freedman's experiments[13] is about −58 kcal mol^{-1}, but Rudnyi's data[13] give only about −24 kcal mol^{-1}. However, theory suggests that the $\Delta H°$ is even less exothermic. The present theoretical value is $\Delta H° = -18.4$ kcal mol^{-1} at the DZP+diff SCF level, and this decreases to −16.5 kcal mol^{-1} at the DZP+diff CISD level. The $\Delta H°$ value is even smaller (−12.9 kcal mol^{-1}) at the DZP CCSD level. Introduction of diffuse functions has little effect at the CISD level, and $\Delta H°$ is only 0.1 kcal mol^{-1} higher at the DZP CISD level relative to the DZP+diff CISD level. Thus $\Delta H°$ at the DZP+diff CCSD level is expected to be around 13 kcal mol^{-1} as well.

In other second row atom cases, basis sets with two sets of d and a set of f functions are needed for truly quantitative energetic predictions. However, for the hydration reaction of PO_3^-, there is not much improvement by using the TZ2P+f basis set (Table VII). The exothermicity for the reaction

$$PO_3^- + H_2O \rightarrow H_2PO_4^- \qquad (6c)$$

is $\Delta H° = -30.3$ kcal mol^{-1} at the DZP+diff SCF level, while $\Delta H° = -30.0$ kcal mol^{-1} at the TZ2P+f SCF level.

While the theoretical $\Delta H°$ values for isomerization reaction 6b at the SCF and the CCSD levels differ by 6 kcal mol^{-1}, this is not so when the "total reaction" 6c including both clustering and isomerization is considered. Inclusion of electron correlation has opposing effects on the theoretical exothermicity for the clustering and isomerization reactions. Thus, the correlation effects are canceled to some extent in the overall reaction 6c and the theoretical results are relatively constant (Table VII). The overall exothermicity ($\Delta H°$) for reaction 6c is 30.0 kcal mol^{-1} at both the DZP+diff SCF and the DZP+diff CISD levels; however, it is 28.0 kcal mol^{-1} at the DZP CCSD level. The small difference increases our confidence in the qualitative reliability of the predicted $\Delta H°$ at the DZP+diff SCF level. This is especially important for the reactions involving more water molecules, where it is only feasible at present to apply the SCF and MP2 methods.

The two-water isomerization

$$PO_3^-\cdot(H_2O)_2 \rightarrow H_2PO_4^-\cdot H_2O \qquad (7a)$$

is more exothermic than the one-water isomerization

$$PO_3^-\cdot H_2O \rightarrow H_2PO_4^- \qquad (6b)$$

(see Table VIII). The exothermicity for the former reaction 7a of $PO_3^-\cdot(H_2O)_2$ is $\Delta H = -21.2$ kcal mol^{-1} at the DZP+diff SCF level, about 3 kcal mol^{-1} higher than that for $PO_3^-\cdot H_2O$ (reaction 6b) at the same theoretical level. The reason is that $H_2PO_4^-$ is 3 kcal mol^{-1} more strongly solvated than PO_3^- (see Section B).

The direct measurement of the exothermicity of the (2,3) hydration reaction

$$PO_3^-\cdot(H_2O)_2 + H_2O \rightarrow H_2PO_4^-\cdot(H_2O)_2 \qquad (8b)$$

(for deuterated species[6]) provides a good opportunity to compare the theoretical with the experimental results. The exothermicity of reaction 8b was measured by Keesee and Castleman in studying the clustering of PO_3^- with water molecules,[6] which process seems to occur spontaneously. As we shall now discuss, the experimental value, $\Delta H° = -16$ kcal mol^{-1} for reaction 8b, is much less exothermic than that suggested by theory (Table VIII).

$$PO_3^-\cdot(H_2O)_3 \rightarrow H_2PO_4^-\cdot(H_2O)_2 \qquad \Delta H° = -20.1 \text{ kcal mol}^{-1} \quad (8a)$$

$$PO_3^-\cdot(H_2O)_2 + H_2O \rightarrow H_2PO_4^-\cdot(H_2O)_2 \qquad \Delta H° = -29.6 \text{ kcal mol}^{-1} \quad (8b)$$

The exothermicity for reaction 8b is -29.6 kcal mol^{-1} at the DZP+diff SCF level. The values for the deuterated species are almost identical, indicating that the isotope effect is of little importance for the reaction. Correlation effects appear relatively unimportant as well. For reaction 6c, the $\Delta H°$ DZP CCSD value is 4 kcal mol^{-1} lower than that at the DZP SCF level. If the difference between the two theoretical levels (SCF and CCSD) for reaction 8a is the same, then the best theoretical $\Delta H°$ estimate for reaction 8b would be -26 kcal mol^{-1}. But this is still 10 kcal mol^{-1} higher than the value observed.[6]

II. The Nature of the Observed (2,3) Hydration Reaction. What (2,3) hydration reaction actually was observed experimentally? We have shown in Section A that both $PO_3^-\cdot(H_2O)_3$ and $H_2PO_4^-\cdot(H_2O)_2$ are expected to be products. Since the two species are indistinguishable mass spectrometrically, both isomers could have been formed. This is consistent with the experimental $\Delta H°$ for the (2,3) hydration reaction and can be rationalized as follows. If $PO_3^-\cdot(H_2O)_3$ and $H_2PO_4^-\cdot(H_2O)_2$ are formed in comparable quantities, the experimental $\Delta H°$ might be higher than that for $PO_3^-\cdot(H_2O)_3$ formation (-9.5 kcal mol^{-1} at the DZP+diff SCF level) and lower than that for $H_2PO_4^-\cdot(H_2O)_2$ formation [for example, for reaction 8b, $\Delta H° = -29.6$ kcal mol^{-1} at the DZP+diff SCF level]. It is clear that the experimental $\Delta H°$ (-16.2 kcal mol^{-1}) is closer to that for the $PO_3^-\cdot(H_2O)_3$ formation reaction.

More support for the conclusion that $PO_3^-\cdot(H_2O)_3$ is a product for the (2,3) hydration reaction appears from the comparison of our theoretical estimate for $\Delta H°$ with the experimental $\Delta H°$ for reaction 11 (as discussed in the last section).

$$H_2PO_4^-\cdot(H_2O)_2 + H_2O \rightarrow H_2PO_4^-\cdot(H_2O)_3 \qquad (11)$$

The experimental[6] $\Delta H°$ for reaction 11 is significantly more exothermic than the value suggested by the present research (less than 8 kcal mol^{-1}, see Section B). The reason may be that the $PO_3^-\cdot(H_2O)_3$ anion is a product together with $H_2PO_4^-\cdot(H_2O)_2$; thus the reactions involving one more water molecule [(3,4) hydration reactions] may include reaction 12, which is highly exothermic.

$$PO_3^-\cdot(H_2O)_3 + H_2O \rightarrow H_2PO_4^-\cdot(H_2O)_3 \qquad (12)$$

Thus the experimentally observed $\Delta H°$ value for the reactions involving four water molecules may be higher than that for the simple clustering reaction 11.

The conclusion that $PO_3^-\cdot(H_2O)_3$ is one of the products for the (2,3) hydration reaction is strengthened when the description of Keesee and Castleman's work[6] is compared with the results found in Viggiano's experiments.[35] Keesee and Castleman call attention to the extraordinary sensitivity of the equilibrium constant of the (2,3) reaction to the applied electric field.[6] This finding may indicate the presence of both $PO_3^-\cdot(H_2O)_3$ and $H_2PO_4^-\cdot(H_2O)_2$, because Viggiano reported that the electric field modifies the clustering ability of the PO_3^- anion.[35]

D. Comparison with Isoelectronic H_2SO_4. Like the $H_2PO_4^-$ anion, the neutral isoelectronic H_2SO_4 molecule prefers C_2 symmetry.[31] The gas electron diffraction and 6-31+G** MP2 geometries[31] agree well except for the SO bond lengths. The longer bond distances (1.623 vs 1.574 Å for S–OH and 1.446 vs 1.422 Å for $S^+–O^-$) found theoretically may be due to basis set incompleteness. The experimental energy for the hydration reaction, $SO_3 + H_2O \rightarrow H_2SO_4$ (-22.1 ± 2.3 kcal mol^{-1}, deduced from the 0 K data in the JANAF tables[36]), can be reproduced at higher levels of theory (e.g., -20.5 kcal mol^{-1} at 6-311 + G(2df,p) MP4SDQ + ZPE) and is only somewhat smaller than the energy predicted here for reaction 6c ($\Delta E_0 = -26.7$ kcal mol^{-1}, at the best level reported in Table VIII).

Like PO_3^-, SO_3 forms a complex with H_2O. However, unlike $PO_3^-\cdot H_2O$, the $SO_3\cdot H_2O$ complex involves *electrophilic* attachment of SO_3 to the water oxygen rather than hydrogen bonding. The theoretical binding energy, about -8 kcal mol^{-1}, is substantially less than that for $PO_3^-\cdot H_2O$ (-12.1 kcal mol^{-1}, see Table VIII). In addition, the computed barrier height for the $SO_3 + H_2O \rightarrow H_2SO_4$ reaction (+17.7 kcal mol^{-1}, based on the separated reactants) is much higher than that reported here for the analogous reaction 6c ($\Delta E_0 = +5.0$ kcal mol^{-1}).

E. Conclusions. The isomerization of $PO_3^-\cdot(H_2O)_n$ clusters (n = 1, 2, and 3) to $H_2PO_4^-\cdot(H_2O)_{n-1}$ has been studied thoroughly, including the barrier heights, theoretical enthalpy changes ($\Delta H°$), and structures and energetics of the product $H_2PO_4^-\cdot(H_2O)_{n-1}$ clusters. The isomerization barrier ($\Delta G^{°\ddagger}$) of $PO_3^-\cdot H_2O \rightarrow H_2PO_4^-$ is 32 kcal mol^{-1} at the DZP+diff SCF level, 25 kcal mol^{-1} at the DZP CISD level, and 21 kcal mol^{-1} at the DZP MP2 level. The isomerization barriers for $PO_3^-\cdot(H_2O)_2$ and $PO_3^-\cdot(H_2O)_3$ are lower by a few kilocalories per mole, due to the (discrete) solvation of the transition state. However, via the six-center mechanism, the barrier ($\Delta G^{°\ddagger}$) is lower by about 5.5 kcal mol^{-1} for the isomerization of $PO_3^-\cdot(H_2O)_2$ at the DZP SCF level. The reaction leading to $H_2PO_4^-\cdot(H_2O)_2$ may occur, through the $PO_3^- + 3H_2O$ reaction, in an environment in which four-body collisions occur with some frequency. Hence the PO_3^- anion may not exist in the aqueous phase, both for thermodynamic and kinetic reasons. However, in the gas phase, theory suggests that $PO_3^-\cdot(H_2O)_3$ is observable, since its isomerization barrier to $H_2PO_4^-\cdot(H_2O)_2$ is relatively high, $\Delta G^{°\ddagger} = 21.8$ kcal mol^{-1} at the DZP+diff MP2 level. A plausible explanation might be the following: (a) the experimental exothermicity for the reaction[6] involving three water molecules is between that for the clustering reaction [$PO_3^-\cdot(H_2O)_3$ formation] and that for the hydration reaction [$H_2PO_4^-\cdot(H_2O)_2$ formation]; and (b) the experimental[6]

---

[35] Viggiano, A. A.; Morris, R. A.; Dale, F.; Paulson, J. F.; Henchman, M. J.; Miller, T. M.; Miller, A. E. S. *J. Phys. Chem.* **1991**, *95*, 1275.

[36] Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*; American Chemical Society: Washington, DC, 1985.

$\Delta H°$ is significantly higher than that suggested by theory for the solvation of $H_2PO_4^-\cdot(H_2O)_2$ to $H_2PO_4^-\cdot(H_2O)_3$.

The global $H_2PO_4^-\cdot(H_2O)_{n-1}$ minima have C_2 symmetry. The energies of the C_s symmetry conformations are about 1 kcal mol^{-1} greater and the C_{2v} structures are higher order stationary points with relative energies about 4 kcal mol^{-1}. In the $H_2PO_4^-\cdot(H_2O)_{n-1}$ structures, the bond distance differences between the $P^+–O^-$ bonds and the P–OH single bonds are inversely related—when one type of bond is lengthened, the other is shortened. This behavior leads to the large difference between the theoretical and experimental structures for $H_2PO_4^-$.

Like PO_3^-, $H_2PO_4^-$ has a tendency to form double-donor double-acceptor hydrogen bonds with H_2O molecules. $H_2PO_4^-$ is more strongly solvated than the PO_3^- and $PO_3^-\cdot H_2O$ anions. The hydration reaction of the PO_3^- anion to give the $H_2PO_4^-$ anion is about 30 kcal mol^{-1} exothermic. This value is similar to that for the formation of $H_2PO_4^-\cdot H_2O$ and of $H_2PO_4^-\cdot(H_2O)_2$, suggesting that the exothermicity does not decrease with the number of water molecules.

The hydration reaction of PO_3^- with a H_2O molecule is only somewhat more exothermic than the comparable hydration reaction of SO_3 with H_2O but involves a much more tightly bound complex and a much lower energy transition state.

Acknowledgment. This research was supported by the U.S. Air Force Office of Scientific Research under Grant AFOSR-92-J-0047. We appreciate helpful suggestions by Drs. Carl Ewig, Michael Henchman, William Jencks, John Paulson, Albert Viggiano, and Frank Westheimer. We thank Drs. Earl M. Evleth and Yundong Wu for the communication of their unpublished results. We thank Dr. Cynthia Meredith for helpful discussions and for several careful readings of the manuscript.