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Theoretical Studies of the Hydration of Metaphosphate with One, Two, and Three Molecules of Water[1]

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Abstract: The reactions of metaphosphate anion (PO_3^-) with one, two, and three molecules of water have been studied theoretically with up to 6-31+G* geometry optimizations and MP4/6-31+G** energy evaluations. H_2O forms a planar six-membered cyclic hydrogen-bonded complex with PO_3^-. The addition of a second H_2O forms a second ring. The calculated complexation enthalpies and entropies for these two processes match reasonably well with those observed experimentally for the gas-phase reactions (Keesee, R. G.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1989,** *111,* 9015). For the addition of a third H_2O, several isomeric complexes have been located. The complex with the H_2O nearly perpendicular to the $PO_3^-(H_2O)_2$ complex is found to be the most stable at each level of optimization. The calculated entropy change with this structure agrees well with the reported value of the third-step hydration in the gas phase. A four-centered transition structure is found for the conversion of the complex to dihydrogen orthophosphate for each reaction. The transition structure involves considerable breaking of one of the water O–H bonds and has a barrier of activation of about 20 kcal/mol with respect to the reactants. For the hydration with two and three water molecules, a six-membered-ring transition structure is also located which is more stable than the four-centered transition structure by several kilocalories/mole.

Metaphosphate, PO_3^-, was first proposed by Westheimer and Bunton about 40 years ago as an intermediate in the aqueous solvolysis of phosphate monoesters, based on the pH–rate profiles.[2] This has attracted tremendous interest because the reaction is one of the most important reactions in biological systems.[3,4] Recent kinetic and stereochemical studies suggest that these reactions do not generate completely free metaphosphate intermediates,[5–7] at least in protic solvents. Experiments in aprotic media have suggested the existence of free metaphosphate.[8,9]

While metaphosphate has been suggested to be extremely reactive in aqueous solution, it is quite stable in the gas phase.[10] For example, Henchman *et al.* reported that it does not react with a variety of nucleophiles such as HCl, H_2O, NH_3, CH_3CN, and $(CH_3)_2O$ in the gas phase[11] and is one of the weakest bases.[12]

Recently, Keesee and Castleman reported the measurement of the standard enthalpy, entropy, and free-energy changes for the successive addition of water or deuterated water to PO_3^- in the gas phase (Table I).[13] They observed that both the enthalpy and entropy changes of the third hydration step ($n = 2$) are quite different from those of the first, second, and fourth hydration steps.[13] They suggested that PO_3^- undergoes simple ion–molecule cluster formation up to the second hydration step but the third hydration step involves an isomerization of the ion–molecule cluster into the dihydrate of the dihydrogen orthophosphate anion ($PO_4H_2^-$). This reaction is rationalized to become facile due to the assumption that additional H_2O molecules reduce the activation energy for the isomerization.[13]

Several questions spring to mind: (1) Why is metaphosphate kinetically stable in the gas phase? (2) What is the effect of additional water molecules ("solvent effect") on the reactivity of PO_3^-? and (3) Why is the third step of the hydration of PO_3^- abnormal?

We report here a theoretical study of the reactions of metaphosphate with one, two, and three water molecules.[14,15] Detailed information about the reaction pathway, geometries of ion–molecule clusters, dihydrogen orthophosphates, and transition structures for the formation of dihydrogen orthophosphates is obtained.

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Table I. Standard Enthalpy, Entropy, and Free-Energy Changes for the Successive Addition of Water to Metaphosphate in the Gas Phase[a]

$$PO_3^-{\cdot}nH_2O + H_2O \rightleftharpoons PO_3^-{\cdot}(n+1)H_2O$$

$(n, n+1)$	$-\Delta H^\circ_{n,n+1}$ (kcal/mol)	$-\Delta S^\circ_{n,n+1}$ (cal/(mol K))	$-\Delta G^\circ_{n,n+1}$ (kcal/mol)
$(0, 1)H_2O$	12.9 ± 0.3	22.2 ± 1	6.3
$(0, 1)D_2O$	12.6 ± 0.2	20.8 ± 1	6.4
$(1, 2)D_2O$	11.4 ± 0.2	22.0 ± 1	4.9
$(2, 3)D_2O$	16.3 ± 0.2	36.3 ± 1	5.5
$(3, 4)D_2O$	11.0 ± 0.4	22.5 ± 1	4.3

[a] Data taken from ref 13.

Results and Discussion

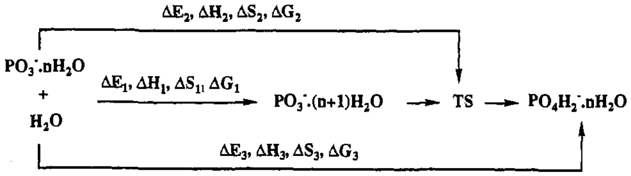
Calculations were performed with Pople's GAUSSIAN88 and GAUSSIAN92 programs.[16] Geometry optimizations were carried out with AM1 and with *ab initio* calculations with the 3-21G* basis set and the 6-31+G basis set to which a set of additional d orbitals was added on the phosphorus. This is referred to as 6-31+G(*). The energies were also evaluated with the MP2/6-31+G* calculations on the 6-31+G(*) geometries. Harmonic vibrational frequency calculations were performed with AM1 and with *ab initio* calculations with the 3-21G* and 6-31+G(*) basis sets. Each transition structure was confirmed to be a saddle point on the potential energy surface from the vibrational frequency calculations. Each cluster or phosphate product corresponds to an energy minimum with no imaginary frequency. For the reaction of PO_3^- with one molecule of water, the geometry optimizations and the frequency calculations were also performed with the 6-31+G* basis set and the energies were evaluated with MP4/6-31+G** calculations.

1. Reaction of PO_3^- with One Molecule of Water. The calculated total energies of the reactants, the ion–molecule cluster, the dihydrogen orthophosphate anion, and the transition structure for the formation of the product are given in Table II. Table IV collects the zero-point energy (ZPE), the thermal energy at 298 °C,[17] and the entropy of these species. In Table V are the calculated relative energies, enthalpies, entropies, and free energy of the cluster, transition structure, and phosphate product with respect to the reactants (see Scheme I).

PO_3^- forms a cyclic ion–molecule cluster with H_2O, as shown by **1**. This is the only stable complex on the potential energy surface, although AM1 calculations also gave an acyclic hydrogen-bonded species.[14] In general, the complexation energy (ΔE_1) calculated by AM1 is too low, while ΔE_1 by 3-21G* is too high. This is also true for the two- and three-water systems. Correlation energy corrections increase the complexation energy by about 2 kcal/mol. The final estimation of enthalpy change (MP4/6-31+G** ΔE_1 with 6-31+G* thermal energy corrections) and the entropy change (ΔS_1, 6-31+G*) for the complexation are −14 kcal/mol and −26.2 cal/mol K (Table V), respectively. These compare quite favorably with the experimental values of −12.8 kcal/mol and −22.3 cal/mol K, respectively.

The transition structure for the conversion of the ion–molecule cluster to the orthophosphate anion is shown by **2**. In this four-centered transition structure, the forming O–P bond is 1.98 Å, about 0.35 Å longer than a O–P single bond. The breaking O–H bond and the forming O–H bond are 1.13 and 1.26 Å, respectively. There is, however, only about 20° of pyramidalization at the P atom. The 3-21G* basis set significantly underestimates the activation energy. The best estimated activation enthalpy (ΔH_2) and entropy (ΔS_2) are about 10 kcal/mol and −35 cal/mol K, respectively, calculated from the reactants PO_3^- and H_2O. The overall free-energy barrier (ΔG_2) is 20.3 kcal/mol, which is sufficiently high to prevent a gas-phase reaction where the concentration of the reactants is low. Because there is a large loss of entropy, the activation barrier is expected to increase with increased temperature. This is in accord with the observed kinetic stability of the metaphosphate anion in the gas phase.[10,11]

Scheme I



The optimized dihydrogen orthophosphate is shown by **3**. The $P(OH)_2$ unit is in a G^+/G^+ conformation to avoid electrostatic repulsion.[18] AM1 and 3-21G* give significantly larger exothermicity compared to other levels of calculations (Table V). The best estimated relative enthalpy (ΔH_3) and entropy (ΔS_3) of this species with respect to the reactants are −23 kcal/mol and −35 cal/mol K, respectively. This further supports the experimental assessment that the first hydration step involves the formation of an ion–molecule cluster rather than a dihydrogen orthophosphate.[13]

2. Ion–Molecule Clusters of PO_3^- with Two and Three Molecules of Water. Starting from **1**, the addition of a second H_2O forms a stable bicyclic structure, **4**. We could not locate any other stable clusters for this system at the 6-31+G(*) level of calculation. The calculated enthalpy and entropy changes of this second hydration step are 11.4 kcal/mol and −29.2 cal/mol K (Table V), respectively. These are in reasonable agreement with Keesee and Castleman's measured values for the second hydration step (Table I).[13] The complexation energy drops slightly at each level of calculations relative to that of the first hydration step because the presence of the first water reduces the negative charge on the third O atom of PO_3^-.

When a third water was introduced, a tricyclic structure, **5**, was first located. The calculated enthalpy and entropy changes for the formation of this structure from **4** are −10.8 kcal/mol and −28.8 cal/mol K, respectively. These values are expected by analogy to those of the first and second steps of hydration but are quite different from the corresponding ones for the third step of hydration shown in Table I.[13]

Several other structures, **6**–**8**, were subsequently located for this trihydrate. In structure **6**, one of the waters is nearly perpendicular to PO_3^-. The two HO bonds of this water are eclipsed with two of the PO bonds and form hydrogen bonds with the two other waters. The two side waters each use one HO bond to form a hydrogen bond.[19] Because of the hydrogen bonding, the perpendicular O becomes more nucleophilic. Structure **7** is similar to **6**, but the perpendicular H_2O is staggered with respect to PO_3^-. The two side waters each form a cyclic structure with PO_3^- but also have hydrogen bonding with the perpendicular H_2O. In structure **8**, the three waters form a cage structure with PO_3^-. Among these structures, structure **6** has the lowest energy at each level of optimization (Table III; AM1, 3-21G*, and 6-31G+G(*)). However, the MP2/6-31+G* calculation with the 6-31+G(*) geometries gave a 7 kcal/mol preference for structure **5** over structure **6**. The calculated geometry of structure

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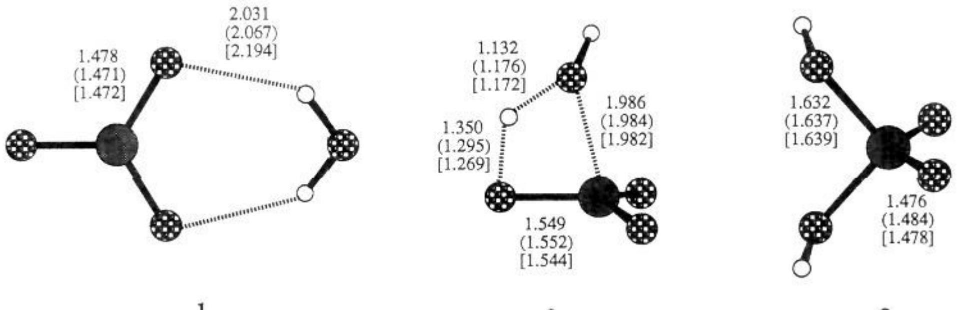
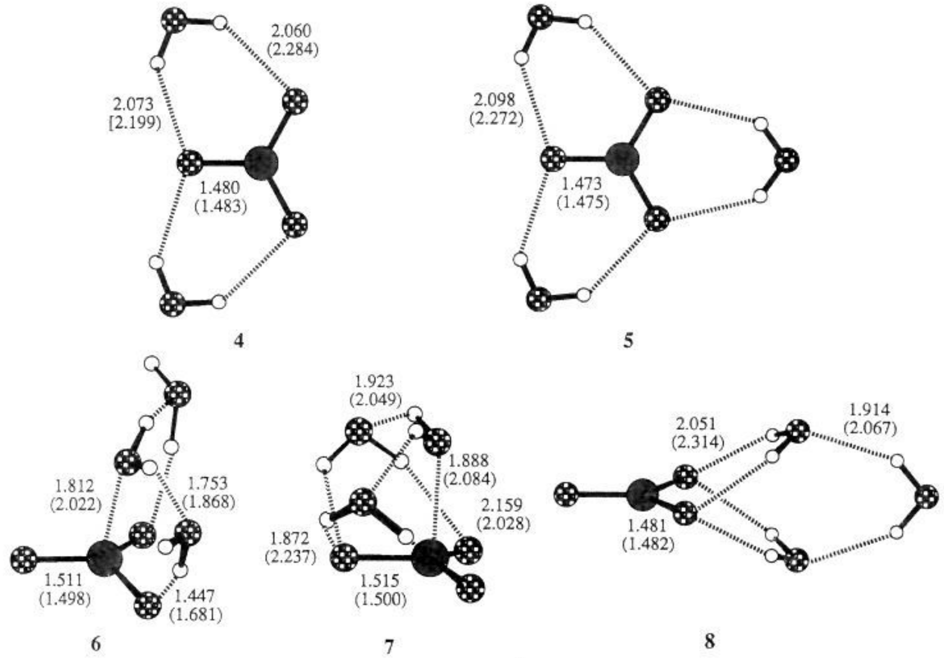
Table II. Calculated Energies (–au) of the Species Involved in the $PO_3^-H_2O$ Hydration Reaction

basis set	PO_3^-	H_2O	$PO_3^-H_2O$	$PO_3^-H_2O$ TS	$PO_2^-(OH)_2$
AM1	0.16318	0.09443	0.27614	0.24800	0.32878
3-21G*	562.55196	75.58596	638.17446	638.15379	638.22377
6-31+G(*)	565.37236	75.99306	641.39014	641.33887	641.42173
6-31+G*//6-31+G(*)	565.43130	76.01774	641.47097	641.41374	641.49638
MP2/6-31+G*//6-31+G(*)	566.10162	76.20874	642.33566	642.29183	642.34983
6-31+G*	565.43152	76.01774	641.47230	641.41845	641.49907
6-31+G**/6-31+G*	565.43152	76.03118	641.48519	641.43306	641.51261
MP2/6-31+G**//6-31+G*	566.09944	76.23262	642.35772	642.31967	642.37584
MP3/6-31+G**/6-31+G*	566.08143	76.23727	642.34421	642.30330	642.36799
MP4/6-31+G**/6-31+G*	566.12576	76.24412	642.39570	642.35593	642.41330



1 2 3

Figure 1. Ion–molecule complex (**1**), transition structure (**2**), and orthophosphate anion (**3**) of the reaction of the metaphosphate anion with one molecule of water. The bond lengths shown are 3-21G*, 6-31+G(*), in parenthesis, and 6-31+G*, in brackets, values, respectively.



4 5 6 7 8

Figure 2. Calculated ion–molecule complexes of the $PO_3^-\cdot 2H_2O$ (**4**) and $PO_3^-\cdot 3H_2O$ (**5–8**) systems. Selected 3-21G* and 6-31+G(*) in parentheses, bond lengths are also shown.

6 is very basis-set dependent while that of structure **5** is much less basis-set dependent. Thus, whether **6** is more stable than **5** energetically still needs further study with higher basis sets and correlation. It is interesting that the calculated loss of entropy for structure **6** is about 16 eu larger than that for structure **5**. The calculated entropy change with structure **6** is not basis-set sensitive and is very close to that reported for the third step of hydration.[20]

While Keesee and Castleman pointed out the possibility of the formation of dihydrogen orthophosphate for the third step of hydration,[13] Schaefer *et al.* suggested that the third step of hydration involves the formation of a mixture of the simple ion–molecule cluster $PO_3^-(H_2O)_3$ (**5**) and the rearranged phosphate product $PO_4H_2^-(H_2O)_2$.[14] Our calculations suggest that the third step of hydration in the gas phase forms a mixture of ion–molecule clusters including **5–8**, with structure **6** dominant. As will be seen in the next two sections, the activation free energy for the formation of $PO_4H_2^-(H_2O)_2$ from structure **4** and one H_2O is too high (about 18 kcal/mol) for the reaction to occur in the gas phase; the formation of $PO_4H_2^-(H_2O)_2$ is too exothermic compared to the experimentally observed enthalpy change.[13] We can easily explain why the fourth step of hydration in the gas phase gives normal enthalpy and entropy changes. The addition of another H_2O to structure **6** has to form another cyclic structure with PO_3^-.

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(20) The calculations systematically give a larger loss of entropy for the formation of the ion–molecule cluster.

Table III. Calculated Total Energies (–au) of the Species Derived from the Reactions of Monophosphate with Two and Three Water Molecules

	AM1	3-21G*	6-31+G(*)	6-31+G* [a]	MP2/6-31+G* [a]
$PO_3^-(H_2O)_2$ (4)	0.38757	713.79262	717.40559	717.50840	718.56709
$PO_3^-(H_2O)_2$ TS (9)	0.36179	713.77659	717.35780	717.45483	718.52715
$PO_3^-(H_2O)_2$ TS (10)			717.38262	717.45964	718.53271
$PO_2^-(OH)_2H_2O$ (13)	0.44096	713.85086	717.44238	717.53798	718.58547
$PO_3^-(H_2O)_3$ (5)	0.49747	789.40712	793.41881	793.54379	794.79617
$PO_3^-(H_2O)_3$ (6)	0.50073	789.44659	793.42001	793.52358	794.78498
$PO_3^-(H_2O)_3$ (7)	0.50340	789.44319	793.41492	793.52998	794.79026
$PO_3^-(H_2O)_3$ (8)		789.41407	793.41506	793.53848	794.79404
$PO_3^-(H_2O)_3$ TS (11)	0.47391	789.39660	793.37520	793.49117	794.75748
$PO_3^-(H_2O)_3$ TS (12)		789.44605	793.40664	793.49855	794.76873
$PO_2^-(OH)_2(H_2O)_2$ (14)	0.55496	789.46992	793.46178	793.57650	794.81954

[a] Calculated with the 6-31+G(*) geometries.

Table IV. Calculated Zero-Point Energy (ZPE, kcal/mol), Thermal Energy (ΔH°_{298}, kcal/mol), and Entropy (S, cal/mol K) of the Species Involved in the $PO_3^-(H_2O)_n$ Hydration Reactions

	AM1			3-21G*			6-31+G*		
species	ZPE	ΔE°_{298}	S	ZPE	ΔE°_{298}	S	ZPE	ΔE°_{298}	S
PO_3^-	5.8	8.4	64.3	8.1	10.3	61.3	7.8	9.9	61.3
H_2O	12.8	14.6	45.1	13.7	15.4	45.1	14.4	16.2	45.0
$PO_3^-H_2O$ (1)	20.5	25.2	87.0	24.8	28.6	78.5	24.7	28.3	80.1
$PO_3^-H_2O$ TS (2)	20.0	23.4	73.8	23.1	26.0	70.8	22.7	25.7	71.3
$PO_2^-(OH)_2$ (3)	22.0	25.9	76.2	25.1	28.3	71.5	25.5	28.7	71.3
$PO_3^-(H_2O)_2$ (4)	35.2	42.0	106.4	41.2	46.8	94.4	40.6	46.7	98.1
$PO_3^-(H_2O)_2$ TS (9)	34.7	40.2	92.2	39.7	44.3	86.3	38.9	43.7	87.2
$PO_3^-(H_2O)_2$ TS (10)							38.6	42.8	81.5
$PO_2^-(OH)_2(H_2O)_2$ (13)	36.7	42.1	88.4	41.9	46.8	86.2	41.4	46.6	88.6
$PO_3^-(H_2O)_3$ (5)	49.6	58.7	123.9	57.4	64.9	108.8	56.8	64.8	114.3
$PO_3^-(H_2O)_3$ (6)	52.9	60.4	110.3	59.1	64.3	89.6	59.2	65.7	99.0
$PO_3^-(H_2O)_3$ (7)	53.2	60.4	104.9	62.0	67.3	89.7	59.5	66.2	101.9
$PO_3^-(H_2O)_3$ (8)				58.9	65.7	102.6			
$PO_3^-(H_2O)_2$ TS (11)	49.4	56.9	111.4	56.5	62.8	100.2	55.3	62.0	104.0
$PO_3^-(H_2O)_2$ TS (12)				57.3	62.2	87.4	55.7	61.4	93.2
$PO_2^-(OH)_2(H_2O)_2$ (14)	51.5	59.7	115.0	58.2	64.9	102.4	58.1	65.1	105.5

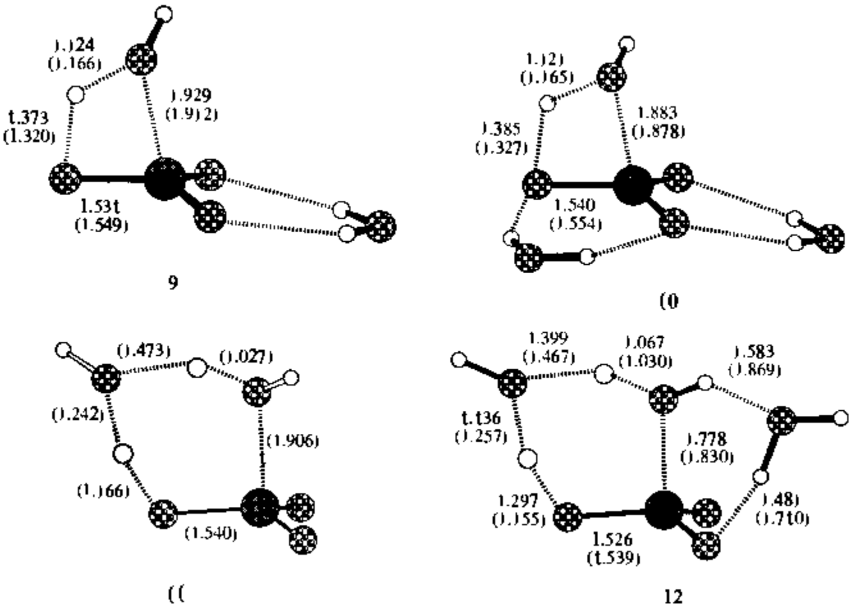

Figure 3. Calculated transition structures for the reactions of the metaphosphate anion with two and three molecules of water. Selected 3-21G* and 6-31+G(*), in parentheses, bond lengths are also shown.

3. Effect of Additional Water Molecules on the Transition Structure for the Formation of the Dihydrogen Orthophosphate Anion. Structures 9 and 10 are calculated four-centered transition structures for the formation of the orthophosphate anion with two and three H_2O molecules, respectively. In these two structures, there is no hydrogen bonding between the reacting H_2O and the nonreacting waters and the nonreacting waters have little effect on the geometry of the four-centered unit.

The best estimated activation enthalpy and entropy are 11.2 kcal/mol and –37.3 cal/mol K for the two-water system and 12.1 kcal/mol and –39.3 cal/mol K for the three-water system. Therefore, the additional water molecules slightly increase the activation energy for the isomerization reaction with the four-centered transition structure.

However, we were able to locate another transition structure with the 6-31+G(*) basis set for the $PO_3^-(H_2O)_2$ reaction, as

Table V. Calculated Changes in the Energy (ΔE, kcal/mol), Enthalpy ($\Delta H°_{298}$, kcal/mol), Entropy (ΔS, cal/mol K), and Free Energy ($\Delta G°_{298}$, kcal/mol) of the Complexation, Activation, and Overall Reaction of PO_3^- with One, Two, and Three Molecules of Water According to Scheme I

basis set	ΔE_1	$\Delta H°_1$	ΔS_1	$\Delta G°_1{}^a$	ΔE_2	$\Delta H°_2$	ΔS_2	$\Delta G_2{}^a$	ΔE_3	ΔH_3	ΔS_3	$\Delta G_3{}^a$
$PO_3^- + H_2O$												
AM1	−11.6	−9.4	−22.4	−2.7	6.1	6.5	−35.6	17.1	−44.7	−41.8	−33.2	−31.9
3-21G*	−22.9	−20.0	−27.9	−11.7	−9.9	−9.7	−35.6	1.0	−53.9	−51.7	−34.9	−41.3
6-31+G(*)	−15.5			−5.5	16.7				−35.2			−22.2
6-31+G*//6-31+G(*)	−13.6			−3.6	16.4				−29.7			−16.7
MP2/6-31+G*//6-31+G(*)	−15.9			−5.9	11.5				−24.8			−11.8
6-31+G*	−14.5	−12.3	−26.2	−4.5	19.4	19.0	−35.0	29.4	−31.3	−28.7	−35.0	−18.3
6-31+G**//6-31+G*	−14.1			−4.1	18.6			28.6	−31.3			−18.3
MP2/6-31+G**//6-31+G*	−16.1			−6.1	9.2			19.2	−26.1			−13.1
MP3/6-31+G**//6-31+G*	−16.0			−6.0	10.5			20.5	−30.1			−17.1
MP4/6-31+G**//6-31+G*	−16.2			−6.2	10.3			20.3	−25.8			−12.8
experimental		−13	−22	−6								
$PO_3^-H_2O + H_2O$												
AM1	−10.7	−8.5	−25.7	−0.8	5.5	5.8	−39.5	17.6[d]	−44.2	−41.9	−34.7	−31.6
3-21G*	−20.2	−17.4	−29.2	−8.7	−10.1	−9.8	−37.3	0.3[d]	−56.8	−54.0	−37.4	−42.9
6-31+G(*)	−14.0	−11.8	−27.0	−3.8	16.0	15.1	−37.9	26.4[d]	−37.1	−35.0	−36.5	−24.1
					(0.4)	(−1.3)	(−43.6)	(11.7)[e]				
6-31+G*//6-31+G(*)	−12.3			−2.1	21.3			31.7[d]	−30.9			−17.8
					(18.2)			(29.5)[e]				
MP2/6-31+G*//6-31+G(*)	−14.2			−4.0	10.9			21.3[d]	−25.8			−12.8
					(7.3)			(18.6)[e]				
experimental		−11	−22	−5								
$PO_3^-{\cdot}2H_2O + H_2O$												
AM1	−13.5	−9.7	−31.5	−0.3[c]	5.1	5.4	−40.0	17.3[f]	−45.3	−42.2	−36.4	−31.4
3-21G*	−42.7	−40.6	−35.3	−30.1[c]	−11.3	−10.7	−39.3	1.0[f]	−57.3	−54.6	−37.1	−43.5
6-31+G(*)	−12.7	−10.8	−28.8	−2.2[b]	14.7	13.8	−39.1	25.5[f]	−39.6	−37.4	−37.6	−26.2
	(−13.4)	(−12.0)	(−44.1)	(1.1)[c]	(−5.0)	(−6.5)	(−49.9)	(8.4)[g]				
6-31+G*//6-31+G(*)	−11.1			−0.6[c]	21.9			32.7[f]	−31.6			−18.2
	(1.6)			(12.9)[b]	(17.3)			(30.7)[g]				
MP2/6-31+G*//6-31+G(*)	−12.8			−2.3[c]	11.5			22.3[f]	−27.4			−14.0
	(−5.7)			(8.8)[c]	(4.5)			(17.9)[g]				
experimental		−16	−36	−6								

[a] The thermal energy and entropy used for the ΔG calculations are those of the corresponding optimized structures. [b] For structure **5**. [c] For structure **6**. [d] For structure **9**. [e] For structure **10**. [f] For structure **11**. [g] For structure **12**.

shown in **11**.[21] Two water molecules are now involved directly in the reaction. This transition structure has small O–H bond breaking on the perpendicular H_2O but significant O–H bond breaking on the second water. It is about 3.5 kcal/mol more stable than the transition structure **9** at the MP2/6-31+G* level. This situation is similar to that found for the hydration of carbonyl compounds, where a six-centered transition structure is more stable than a four-centered transition structure.[22]

For the reaction with three water molecules, a similar transition structure, **12**, was located with both the 3-21G* and 6-31+G(*) basis sets. This structure is very similar to structure **6** with the 3-21G* basis set, and there is only a 0.3 kcal/mol energy difference between the two structures. With the 6-31+G(*) basis set, the transition structure is more advanced and has a higher activation energy. The transition structure is 7 kcal/mol more stable than the transition structure **10** at the MP2/6-31+G* level of calculation. The calculated activation free energy for the third step of hydration is about 18 kcal/mol, which is still too high for the isomerization to occur in the gas phase.

4. Effect of Hydration on the Formation of the Dihydrogen Orthophosphate Anion. Structures **13** and **14** are dihydrogen orthophosphate hydrated by one and two molecules of water, respectively. Both **13** and **14** have C_2 symmetry. While **13** is the global minimum for the two-water system, we are not quite certain whether **14** is the global minimum for the three-water system, since many isomeric structures are possible and a thorough search was not carried out. This does not affect our subsequent discussion. The hydration has little effect on the orthophosphate geometry. The exothermicities (ΔE_3) for the formation of **13** and **14** from **1** and **4** are 25.8 and 27.4 kcal/mol, respectively. We expect these reaction energies to be slightly higher with higher levels of calculations, based on the calculations for the $PO_3^-H_2O$ reaction. Therefore, the reaction enthalpy increases as orthophosphate is more hydrated. This is likely due to reduced electrostatic interactions by the presence of the water molecules.

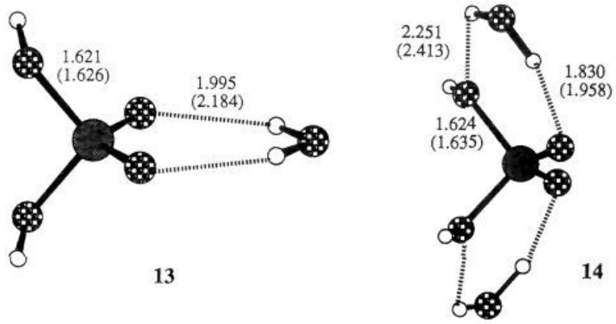

Figure 4. Calculated orthophosphate products for the reactions of the metaphosphate anion with two and three molecules of water. Selected 3-21G* and 6-31+G(*), in parentheses, bond lengths are also shown.

The calculated reaction entropy (ΔS_3) for the formation of **12** is about −35 kcal/mol K. This is the same as the measured entropy change of the third step of hydration reported by Keesee and Castleman.[13] However, the calculated enthalpy for the formation of **14** is about −25 kcal/mol with MP2/6-31+G* level and is significantly larger than that measured for the third step of hydration, which is −16 kcal/mol. Therefore, it is quite unlikely that the measured abnormal enthalpy and entropy for the third step of hydration are due to the formation of hydrogen orthophosphate.

Summary

We found that in the gas phase, metaphosphate forms simple ion–molecule clusters with one and two molecules of water. With

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[21] We were unable to locate this transition structure with the AM1 and the 3-21G* basis sets.

[22] Fraser, R. R.; Kong, F.; Stanciulescu, M.; Wu, Y.-D.; Houk, K. N. *J. Org. Chem.* **1993**, *58*, 4431.

more than three molecules of water, a $PO_3^-(H_2O)_n$–H_2O adduct can also be formed, where one of the waters is nearly perpendicular to PO_3^- and behaves as a nucleophile. This structure has been proposed to be an intermediate in the solution hydrolysis of monoester monoanion phosphates.[2] Thus, the stepwise hydrations of metaphosphate in the gas phase studied by Keesee and Castleman stop at the formation of ion–molecule clusters, and the formation of dihydrogen orthophosphate does not occur. This is supported by the facts that (1) the calculated activation free energy for the reaction (18 kcal/mol) is too high for a gas-phase reaction and (2) the exothermicity of the formation of orthophosphate is much larger than the experimentally measured enthalpy changes.

The formation of orthophosphate for the $PO_3^-H_2O$ system occurs with a four-centered transition structure, **2**. The activation energy with respect to separated PO_3^- and H_2O is about 20 kcal/mol. With two or more water molecules, a six-centered transition structure is more favorable than a four-centered transition structure. This six-centered transition structure might be similar to that of the hydrolysis of monoester monoanion phosphate in aqueous solution.

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