Hydration in the Gas Phase of the Orthophosphate Anion, $(HO)_2PO_2^-$, and the Conversion of the Orthophosphate to the Metaphosphate, PO_3^-, Ion

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Abstract: The orthophosphate anion, $(HO)_2PO_2^-$, was produced in the gas phase by electrospray. The hydration equilibria $(HO)_2PO_2^-(H_2O)_{n-1} + H_2O = (HO)_2PO_2^-(H_2O)_n$ were determined after transfer of the ions into a reaction chamber containing known partial pressures of H_2O, where thermal conditions prevailed. The $\Delta G^\circ_{n-1,n}$, $\Delta H^\circ_{n-1,n}$, and $\Delta S^\circ_{n-1,n}$ for steps $(n-1,n) = (0,1)$ and $(1,2)$ were obtained from equilibrium measurements in the 20−150 °C range. The ion concentration ratio was determined mass spectrometrically. The thermochemical data obtained are in good agreement with recent theoretical calculations. Under some conditions of the experiments, the equilibria $(HO)_2PO_2^-(H_2O)_n = PO_3^-(H_2O)_{n-1} + H_2O$ should have been observed according to reports in the literature. However, the formation of the metaphosphate ion, PO_3^-, and its hydrates was not observed. In separate experiments with a different apparatus setup, the kinetic energy threshold for the collision-induced decomposition $(HO)_2PO_2^- = PO_3^- + H_2O$ was determined. The activation energy barrier obtained was high. The significance of these results to the possible conversion of the orthophosphate to metaphosphate, when a few hydrating molecules are available, is discussed.

Introduction

Recently, we described[1] an ion source reaction chamber with which ion−molecule equilibria involving Electrospray produced ions can be determined in the gas phase. An investigation involving the hydration of some 50 singly and doubly charged anions deriving from oxo acids of C, N, S, P, Cl, Br, and I was completed more recently.[2] The Electrospray method is of particular importance for the generation of gas phase ions which cannot be produced by conventional methods.[3] The orthophosphate is such an ion.

The orthophosphate ion $(HO)_2PO_2^-$ and its hydration are of special interest because of the importance of phosphates in biological systems. In the present work the hydration equilibria

$$(HO)_2PO_2^-(H_2O)_{n-1} + H_2O = (HO)_2PO_2^-(H_2O)_n \quad (1)$$

for $(n-1,n) = (0,1)$ and $(1,2)$ could be determined over a temperature range between 20 and 150 °C. The thermochemical data obtained for $\Delta G^\circ_{n-1,n}$, $\Delta H^\circ_{n-1,n}$, and $\Delta S^\circ_{n-1,n}$ are of interest in their own right as will be shown in the Results and Discussion section. However, it was realized in the course of this work that the experimental observations also have a bearing on the conversion of orthophosphate $(HO)_2PO_2^-$ to metaphosphate, PO_3^-, and *vice versa*, which is mediated by the presence of hydration by a few or several water molecules.

The role of the metaphosphate ion PO_3^- as an intermediate in the aqueous solvolysis of phosphate monoesters and other related reactions in solution has been the subject of intense discussion.[4] Central to these has been the extent to which a free metaphosphate ion is formed.[4c] More recently, there have been attempts to contribute relevant information on the basis of gas phase ion−molecule reaction studies involving the PO_3^- ion. Henchman and co-workers[5] were the first gas phase ion chemistry group to do such work. These authors found the PO_3^- ion to be relatively unreactive in the gas phase. In particular, they found that the conversion of this ion to the orthophosphate,

$$PO_3^- + H_2O = (HO)_2PO_2^- \quad (2)$$

did not occur. However, the experimental conditions used[5] were such that the reaction would have been observed only if it did have an activation energy barrier which was smaller than a few kcal/mol.

Much less restrictive conditions were available in a later study by Keesee and Castleman[6] which reported a gas phase study of the hydration equilibria

$$PO_3^-(H_2O)_{n-1} + H_2O = PO_3^-(H_2O)_n \quad (3)$$

which were determined with a high-pressure mass spectrometer over a wide temperature range. These authors observed some anomalies in the hydration data obtained which led them to the conclusion that a conversion of the metaphosphate to the orthophosphate occurs in the third hydration step.

$$PO_3^-(H_2O)_2 + H_2O = (HO)_2PO_2^-(H_2O)_2 \quad (4)$$

The authors[6] also came to the conclusion that they were

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(1) (a) Klassen, J. S.; Blades, A. T.; Kebarle, P. *J. Am. Chem. Soc.* **1994**, *116*, 12075. (b) Klassen, J. S.; Blades, A. T.; Kebarle, P. *J. Phys. Chem.* In press.

(2) Blades, A. T.; Klassen, J. S.; Kebarle, P. *J. Am. Chem. Soc.* In press.

(3) (a) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 455. (b) Keesee, R. G.; Castleman, A. W. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1011. (c) Bartness, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. II, p 1.

(4) (a) Westheimer, F. H. *Science* **1987**, *235*, 1173. (b) Westheimer, F. H. *Chem. Rev.* **1981**, *81*, 313. (b) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161. (c) Freeman, S.; Friedman, J. M.; Knowles, D. *J. Am. Chem. Soc.* **1987**, *109*, 3166.

(5) Henchman, M.; Viggiano, A. A.; Paulson, J. F.; Freedman, A.; Wormhoudt, J. *J. Am. Chem. Soc.* **1985**, *107*, 1453.

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

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observing the equilibrium of reaction, eq 4. Assuming that these conclusions were correct, the present experiments dealing with the hydration of the orthophosphate (see eq 1) should lead also to formation of metaphosphate by the reverse of eq 4. The outcome of our search for the PO_3^- ion and the consequences are described in the Results and Discussion section.

Experimental Section

(a) Hydration Reactions and Equilibria. The hydration reaction and equilibria were determined with apparatus which has been described in detail.[1b] Therefore, only the main features will be given here.

A solution containing ~10^{-4} mol/L of the sodium phosphate in methanol solvent was infused through the Electrospray capillary, at ~1 μL/min flow rate, by means of a motor driven syringe. The Electrospray capillary which is at high negative voltage (−4.5 kV) emits a spray of droplets which are negatively charged due to an excess of anions over cations in the droplets. Droplet evaporation in the atmosphere leads to gas phase negative ions. Part of the spray is sucked in by a second capillary (−40 V) leading to a chamber maintained at 10 Torr. The gas jet and ions entering the low-pressure chamber passes through an electric field which deflects the ions into a reaction chamber (−17 V). A gas mixture of 10 Torr of bath gas, N_2, and a known partial pressure of water flows through the reaction chamber. Ion equilibria are established in this chamber and the relative ion concentrations are determined by letting a fraction of the gas and ions escape, through an orifice (−3 V), into a vacuum chamber which houses a triple quadrupole mass spectrometer.

The apparatus described previously[1b] operated only at room temperature. The ion reaction chamber used in the present work incorporated heaters and afforded determinations over a temperature range extending from 20 to +180 °C. Full documentation of this ion source is given elsewhere.[7]

(b) Determination of the Kinetic Energy Thresholds for Collision-Induced Decomposition (CID). The apparatus and method used for the determination of the CID thresholds have been described in detail.[8] Only a brief description and information specific to the present measurements will be given here.

Ions produced by Electrospray at 1 atm are admitted by means of a capillary into a chamber maintained at ~10 Torr. The ions are sampled *via* a 100 μm diameter orifice which leads to the vacuum chamber and the triple quadrupole mass spectrometer. The first few electrodes past the orifice are at potentials very close to that of the orifice in order to avoid collision-induced excitation of the ions in this relatively high gas density region. The precursor ions, such as $(HO)_2PO_2^-$, are mass selected with the first quadrupole mass spectrometer, Q_1. The precursor ions are then accelerated between Q_1 and Q_2 by a known potential drop. Collision gas argon is present in the Q_2 space and Q_2 is operated in the AC only mode which transmits all ions. The precursor ions and product ions produced by CID in Q_2 are mass analyzed in Q_3 and detected with an ion counting device.

The threshold curves, see Figure 5 in Results and Discussion, are plots of the CID product ion intensity *versus* the kinetic energy of the collision between the precursor ion and the collision gas, in the center of mass frame. The threshold energy, E_o, is obtained from such plots by a curve-fitting procedure. We have used the CRUNCH curve-fitting program developed by Armentrout and co-workers.[9]

In order to obtain reliable determinations three major conditions must be met: (a) The precursor ions entering Q_2 must have a known internal energy distribution such as Maxwell Boltzmann distribution at a known temperature. (b) The translational kinetic energy distribution of the precursor ions should be relatively narrow. (c) The product ions should be formed from precursor ions which have experienced only a single collision with the collision gas, i.e., the collision gas pressure should be sufficiently low to lead to single-collision conditions.

It was found that in our apparatus[8] for Electrospray ions, some collisions of the ions with neutral gas, originating from the sampling orifice, occur in Q_1. It could be demonstrated that this involves ions accelerated by the radial DC field in Q_1. These collisions lead to a spread in the velocity distribution of the precursor ions, as measured by a retarding offset potential on Q_2 in the absence of collision gas. The velocity spread is minimized by working at low radial DC potentials in Q_1, i.e. at low mass resolution. Experimentation since our previous publication[8] has shown that the velocity spread could be further reduced by decreasing the residence time of the ions in Q_1. The optimum conditions were observed for an acceleration potential of ~15 V between the sampling orifice and Q_1. For such conditions, the orthophosphate anion, $m/z = 97$, has an approximately Gaussian velocity distribution with a fwhm of ~0.6 eV laboratory scale. The product ion (PO_3^-) showed a minimum tailing toward low energies for approximately the same conditions. Low collision gas pressures (0.06 mTorr) were used. Threshold curves obtained with 0.12 and 0.06 mTorr of argon as the collision gas, gave thresholds increasing by less than 0.15 eV.

The determinations were facilitated by the relatively good yields of the orthophosphate ions obtained with Electrospray. Thus, the $(HO)_2PO_2^-$ ion after mass analysis had an intensity of ~20 000 counts/s. This ion could be produced by Electrospray in high yields where it represented ~80% of the total ion intensity. The ion was quite isolated—nearest mass ions occurred some 8 mass units away and had minor intensities. These conditions allowed one to use low-mass resolution in Q_1.

Results and Discussion

(a) Hydration Energies of the Orthophosphate Ion $(HO)_2PO_2^-$. The hydration energies of the orthophosphate ion,

$$(HO)_2PO_2^-(H_2O)_{n-1} + H_2O = (HO)_2PO_2^-(H_2O)_n \quad (1)$$

were determined for $n = 1$ and 2 by measurements of the equilibrium constants and their temperature dependence.

As in previous work,[1,2] the equilibrium constants $K_{n-1,n}$ are obtained from determinations of the ion intensity ratio, I_n/I_{n-1}, with a mass spectrometer, see Experimental Section. This ratio is assumed to be equal to the ion concentration ratio in the ion equilibration chamber. The equilibrium expression

$$K_{n-1,n} = \frac{[(HO)_2PO_2^-(H_2O)_n]}{[(HO)_2PO_2^-(H_2O)_{n-1}]P_{H_2O}} \quad (5)$$

requires that a plot of I_n/I_{n-1} *versus* P_{H_2O} should lead to a straight line which passes through the origin. The slope in these plots corresponds to the equilibrium constant.

Three plots for the (0,1) equilibria at three different temperatures are shown in Figure 1. The equilibrium constants obtained from the slopes of such plots were used to obtain the van't Hoff plots shown in Figure 2, which lead to the enthalpy, $\Delta H°$, free energy, $\Delta G°$, and entropy change, $\Delta S°$, for the (0,1) equilibrium given in Table 1. Similar determinations were obtained also for the 1,2 reaction and the corresponding thermodynamic quantities are given in Table 1.

The thermodynamic values for the hydration of the metaphosphate ion, PO_3^-, obtained by Keesee and Castleman[6] are also quoted in Table 1.

The present experimental results can be compared with values obtained in the theoretical study by Wu and Houk,[10] see Table 1. It is found that the agreement is excellent for the $\Delta G°$ values at 298 K while the theoretical $-\Delta H°$ and $-\Delta S°$ values are somewhat higher. Actually, these differences can be expected. The theoretical values are based on lowest electronic energy

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[7] Blades, A. T.; Klassen, J. S.; Kebarle, P. In preparation.

[8] Anderson, S. G.; Blades, A. T.; Klassen, J.; Kebarle, P. *Int. J. Mass Spectrom. Ion Processes* **1995**, *141*, 217.

[9] (a) Armentrout, P. B. Thermochemical Measurements by Guided Beam Mass Spectrometry. *Advances in Gas Phase Ion Chemistry*; Adams, N., Babcock, L. M., Eds.; JAI Press Inc.: Greenwich, 1992; Vol. 83, p 1. (b) Dalleska, N. F.; Honma, K.; Armentrout, P. B. *J. Am. Chem. Soc.* **1993**, *115*, 12125.

[10] Wu, Y. D.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 11997.

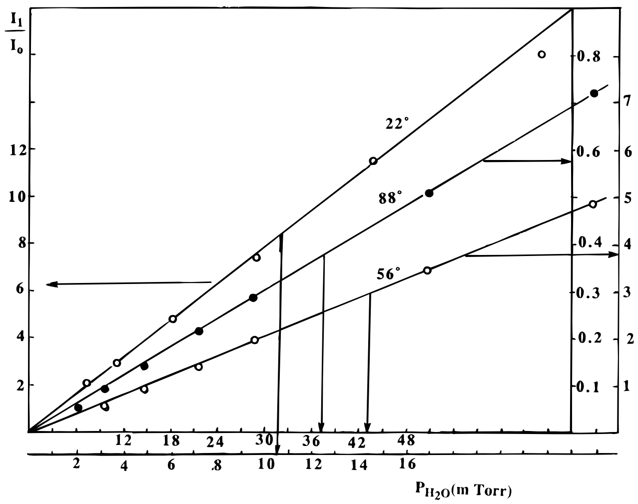


Figure 1. Plot of ratio of ion intensities I_1/I_0 for the $(HO)_2PO_2^-(H_2O)$ and $(HO)_2PO_2^-$ ions versus the partial pressure of water, P_{H_2O}, in mTorr. At equilibrium, $(HO)_2PO_2^- + H_2O = (HO)_2PO_2^-(H_2O)$, plots should lead to straight lines with slope equal to the equilibrium constant $K_{0,1}$, see eq 5. Three plots are shown obtained at three different temperatures, 22, 56, and 88 °C. The equilibrium constants obtained at these temperatures are 594800, 51700, and 7600 (atm^{-1}).

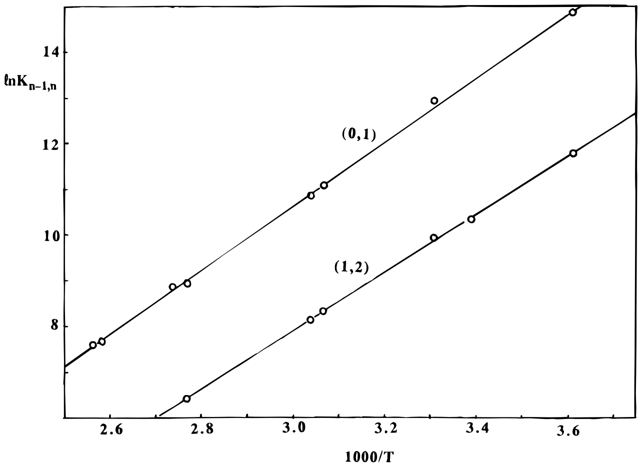
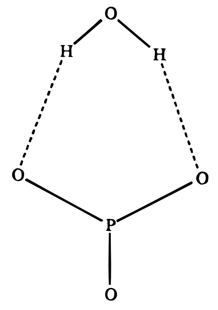


Figure 2. van't Hoff plots of equilibrium constants $K_{0,1}$ and $K_{1,2}$ for hydration of $(HO)_2PO_2^-$, eq 5.

structures where one water molecule forms two hydrogen bonds to the phosphate ion, see the analogous structure **1** for the PO_3^- monohydrate. However, the singly H bonded structure **2**, which



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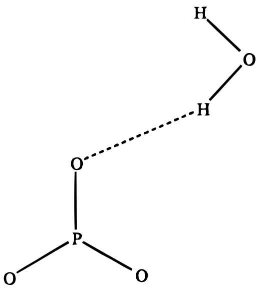

2

leads to lower $-\Delta H$ and $-\Delta S$ values, becomes more stable at higher temperatures where the more favorable entropy, due to the looser bonding, becomes more important. Calculations for the monohydrate of NO_3^- by Schaefer and co-workers[11] predict that the single H bonded structure is electronically less stable by ~2.2 kcal/mol. Vibrational frequencies provided for the structures allow one to estimate that the single bonded structure has a higher entropy, ~7 cal (deg/mol), relative to the two H bond structure. These data indicate that the two structures will have near equal free energies near room temperature, while the single bonded structure will become more stable at higher temperatures. Similar differences may be expected also for the PO_3^- and the $(HO)_2PO_2^-$ hydrate. The van't Hoff plots in the experimental determinations for these species extend to higher temperatures where the single H bonded structure is expected to become dominant. The lower $-\Delta H°$ and $-\Delta S°$ values observed in the experimental determinations for (0,1) and (1,2) [PO_3^-, Keesee,[6] and $(HO)_2PO_2^-$, present work] in Table 1 are thus in line with the expected contribution of the looser single H bond structures.

Table 1. Hydration Energies of the Orthophosphate $(HO)_2PO_2^-$ and the Metaphosphate Anions[a]

ion	$(n-1,n)$	$-\Delta H°$, kcal/mol	$-\Delta S°$, cal/(deg mol)	$-\Delta G°_{298}$, kcal/mol
$(PO_3^-)^b$	(0,1)	12.6 (12.3)[d]	20.8 (26.2)[d]	6.4 (4.5)[d]
	(1,2)	11.4 (11.8)[d]	22.0 (27)[d]	4.9 (3.8)[d]
	(2,3)[c]	16.3[c]	36.4[c]	5.5[c]
$(HO)_2PO_2^-$	(0,1)	14.0 (15.8)[d]	21.0 (27)[d]	7.7 (7.5)[d]
	(1,2)	12.3 (14.2)[d]	20.8 (28)[d]	6.1 (5.8)[d]

[a] Estimated errors for present results: $\Delta H = \pm 1$ kcal/mol, $\Delta S° = \pm 4$ cal/(deg mol), $\Delta G°_{298} = \pm 0.5$ kcal/mol. [b] Experimental data for PO_3^- are from Keesee and Castleman.[6] [c] The 2,3 hydration value for PO_3^- is anomalous and assumed to reflect a simultaneous conversion to orthophosphate.[6] [d] Theoretical results by Wu and Houk[10] in parentheses.

Lower binding energies for the PO_3^- relative to the $(HO)_2PO_2^-$ for the mono- and dihydrate are observed in Table 1. This result is in general agreement with determinations[2] involving other oxo anions which show that anions for which the charge is delocalized over a larger number of equivalent oxygen atoms lead to lower hydration energies. In the present case, the PO_3^- ion for which the charge is delocalized over three equivalent oxygen atoms hydrates less strongly than the $(HO)_2PO_2^-$ ion where there are only two equivalent oxygens.

(b) Conversion of Hydrates of the Metaphosphate Ion, $PO_3^-(H_2O)_n$, to the Orthophosphate Ions, $(HO)_2PO_2^-(H_2O)_{n-1}$. A decrease of $-\Delta H°_{n-1,n}$ with increasing n has been observed in all gas phase hydration studies of singly charged ions.[3a,b] In the absence of specific valence bonding interactions such a decrease is expected since the charge becomes gradually more delocalized over the solvent molecules and also the space near the ion may become more restricted. The observation by Keesee and Castleman[6] that for PO_3^- the value for $-\Delta H_{2,3}$ is considerably larger than the values for $-\Delta H°_{0,1}$ and $-\Delta H°_{1,2}$, see Table 1, must indicate a special process. As mentioned in the Introduction, the authors[6] assumed that a conversion of meta- to orthophosphate occurs when the third water molecule is added.

$$PO_3^-(H_2O)_2 + H_2O = (HO)_2PO_2^-(H_2O)_2 \qquad (4)$$

The conversion of the metaphosphate to the orthophosphate, see eq 2, is expected to be quite exothermic and this process could be responsible for the larger exothermicity observed for the third water molecule. The data indicated also that the reaction in eq 4 and subsequent hydration steps remain in equilibrium.[6]

At equilibrium one should be able to observe the same ion concentration ratios including the formation of the PO_3^- ion if one started with the orthophosphate $(HO)_2PO_2^-$ ion. The idea

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(11) Shen, M.; Xie, Y.; Schaefer, H. F. *J. Chem. Phys.* **1990**, *93*, 3379.

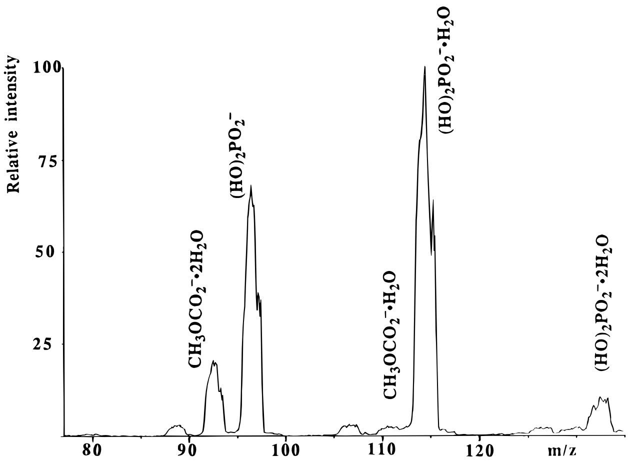

Figure 3. Observed ion intensity distribution in a reaction mixture containing the orthophosphate ion $(HO)_2PO_2^-$ and H_2O vapor at 92 m Torr partial pressure. Bath gas N_2, 10 Torr, temperature 352 K. The metaphosphate PO_3^- ion at $m/z = 79$ is not observed. Had a conversion of $(HO)_2PO_2^-$ hydrates to PO_3^- hydrates occurred and reached equilibrium, unhydrated PO_3^- ion should have been formed by the reverse of (4) followed by equilibria, eq 3, at a yield of ~82% of the total ion intensity. The ions at $m/z = 93$ ($CH_3OCO_2^- \cdot H_2O$) and $m/z = 111$ ($CH_3OCO_2^- \cdot 2H_2O$) are often observed[12] and are formed by Electrospray due to a sodium bicarbonate impurity in the salts used and the methanol solvent. The last visible ion below $m/z = 93$ is at $m/z = 89$.

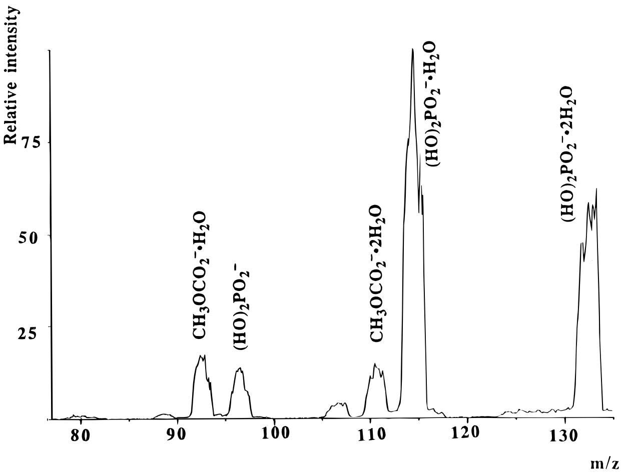

Figure 4. Same as Figure 3, but for conditions $P_{H_2O} = 795$ mTorr and 352 K. The unhydrated PO_3^- ion intensity at $m/z = 79$ predicted by equilibria, eq 3 and eq 4, should have been ~30% of the total ion intensity, but no ion intensity is observed at $m/z = 79$.

to perform a check on the hydration equilibria converting the metaphosphate to the orthophosphate by starting with the orthophosphate ion arose during our measurements of the hydration equilibria of the orthophosphate anion. A special search for the PO_3^- ion was made by selecting conditions for which this ion should have been an abundant product in the equilibrium system as predicted by the results of Keesee and Castleman.[6] The $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$ data[6] allow one to evaluate the relative ion concentrations for any given temperature and H_2O partial pressure in the temperature range used.[6] Because Keesee and Castleman[6] deduced that the equilibrium, eq 4, establishes relatively more slowly than the other hydration equilibria, one should also work at relatively high H_2O partial pressures, similar to the pressures that they used.

The mass spectra shown in Figures 3 and 4, obtained with $(HO)_2PO_2^-$, illustrate some typical results under such conditions. The ion intensities shown in Figure 3, obtained at 352 K and with 92 mTorr of H_2O vapor, show that the PO_3^- ion, mass to charge ratio $m/z = 79$, is absent. The major ions observed are at $m/z = 97$ for $(HO)_2PO_2^-$, $m/z = 115$ for $(HO)_2PO_2^-(H_2O)$, and $m/z = 133$ for $(HO)_2PO_2^-(H_2O)_2$. The intensities predicted on the basis of the PO_3^- hydration equilibria[6] would have been as follows: PO_3^-, ~82%; $PO_3^-(H_2O)$ and $(HO)_2PO_2^-$, ~18%; $PO_3^-(H_2O)_2$ and $(HO)_2PO_2^-(H_2O)$, ~0.4%. It should be noted that $PO_3^-(H_2O)_n$ have the same mass to charge ratio, m/z, as the $(HO)_2PO_2^-(H_2O)_{n-1}$ ions and cannot be distinguished mass spectrometrically. We have assigned the ions in our mass spectrum as $(HO)_2PO_2^-(H_2O)_n$, because PO_3^- is absent. The PO_3^- cannot be present in our spectra only as PO_3^- hydrates because under the conditions used, PO_3^- is predicted[6] to be the major ion, on the basis of the (0,1) and (1,2) equilibria for this ion, see Table 1.

A higher partial pressure of H_2O at 795 mTorr at the same temperature, 352 K, led to the data shown in Figure 4. The intensities predicted on the basis of the PO_3^- hydration equilibria[6] are the following: PO_3^-, ~29.2%; $PO_3^-(H_2O)$ (and $(HO)_2PO_2^-$), ~57.8%; $PO_3^-(H_2O)_2$ (and $(HO)_2PO_2^-(H_2O)$), ~11.2%; higher hydrates, ~1.7%. The mass spectra show no intensity at $m/z = 79$, i.e., no PO_3^- ions, and therefore the observed intensities at $m/z = 97$, 115, and 133 can be attributed to the $(HO)_2PO_2^-$ ion and its hydrates.

A series of experiments at lower and intermediate pressures, at 352 K, also provided mass spectra where the PO_3^- ion was absent. This was also the case at lower temperatures such as 300, 335, and 342 K.

The absence of PO_3^- in the above experiments casts very serious doubt about the presence of equilibration in reaction 4.

(c) Experimental Determination of the Energy Barrier for Conversion of the Orthophosphate to the Metaphosphate from Kinetic Energy Thresholds for the Collision-Induced Decomposition of $(HO)_2PO_2^-$. In the previous section, results were presented which showed that the production of metaphosphate hydrates from orthophosphate hydrates, by reactions such as the reverse of eq 4, could not be observed under thermal conditions at ~80 °C and lower temperatures. This suggests that the conversion has an appreciable activation energy barrier. The present experiments describe attempts to obtain estimates for the magnitude of the barrier.

The orthophosphate ion $(HO)_2PO_2^-$ produced in the same ion source as used for the equilibria was subjected to collision-induced dissociation (CID) with argon as the collision gas, in a triple quadrupole mass spectrometer. The desired ion exiting the ion source was mass selected with quadrupole Q_1. The collisions occurred in Q_2 at very low Ar pressures such that single-collision conditions prevailed and the dissociation product ions were detected with Q_3. Details concerning the apparatus and method are given in the Experimental Section.

The experimentally determined threshold curve for the product ion PO_3^- from the collision-induced decomposition of the $(HO)_2PO_2^-$ ion is shown in Figure 5. The internal energy difference between the orthophosphate and the transition state TS, predicted by this measurement, can be obtained by curve-fitting procedures. We have used the Armentrout[9] CRUNCH program. The values obtained are

$$(HO)_2PO_2^- \rightarrow TS \rightarrow PO_3^- + H_2O \tag{6}$$

$$\text{(a) } \Delta E_6^\ddagger = 52.9 \text{ kcal/mol}$$

$$\text{(b) } \Delta E_6^\ddagger = 54.7 \text{ kcal/mol (0 K); } 54.5 \text{ kcal/mol (298 K)}$$

$$\text{(c) } \Delta E_6^\ddagger = 53.7 \text{ kcal/mol (298 K) (kinetic shift)}$$

The internal energy change in (a) is obtained from a fit to the

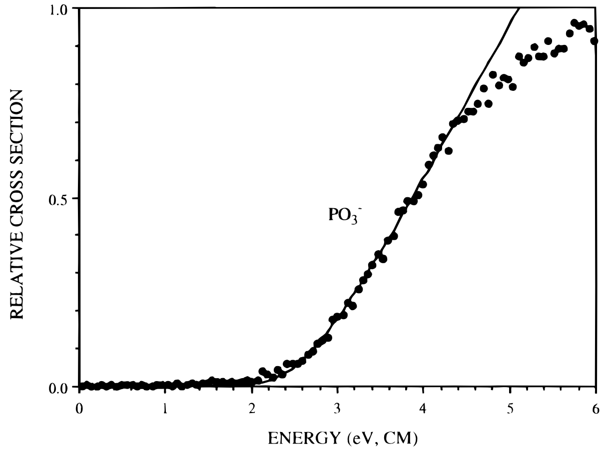

Figure 5. Kinetic energy transfer for collision-induced decomposition of the orthophosphate ion: $(HO)_2PO_2^- \rightarrow PO_3^- + H_2O$. Collision gas Ar. Kinetic energy in electron volts in the center of mass frame. The fitting procedures using Armentrout's CRUNCH led to internal energy changes for decomposition shown in eq 6. The best fit parameters obtained were $n = 1.7$, $m = 1$.

data which does not take into account that the internal energy present in the precursor ion before the collision may contribute to the energy required for the process. The value in (b) represents the energy change where both precursor ion and products are at the same, stated, temperature. It is based on a data-fitting procedure which assumes that the precursor ion is at 298 K but the products observed at the threshold are much cooler (~0 K).[9] The $\Delta E^\ddagger$ value given above is then evaluated from a thermochemical cycle involving the heat capacities of precursor and products. The value in (c) represents the energy change at 298 K; however, the fitting procedure[9] corrects for the kinetic shift.[12,13]

The vibrational frequencies for the precursor ion and the transition state are required for the fits (b) and (c). We have used the vibrational frequencies obtained by Wu and Houk.[10,14] The differences between the values obtained with procedures (a), (b), and (c) are very small and a value of ~54 kcal/mol can be chosen.

The findings of Keesee and Castleman[6] stimulated theoretical work by Schaefer *et al.*[15] and Wu and Houk.[10] In particular, Wu and Houk[10] evaluated the energies of the reactants including that of the transition state for the reactions leading to conversion to the orthophosphate

$$PO_3^-(H_2O)_n + H_2O \rightarrow (TS)_n = (HO)_2PO_2^-(H_2O)_n \quad (7)$$

$$\text{for } n = 0, 1, 2$$

A schematic diagram of the energy changes for $n = 0$ and the structures of the reactants obtained by Wu and Houk is shown in Figure 6. The reaction is predicted to have an activation barrier, $\Delta E^\ddagger = 9.9$ kcal/mol. This represents a distinction from simple hydration and other simple clustering reactions which generally have no activation barriers.

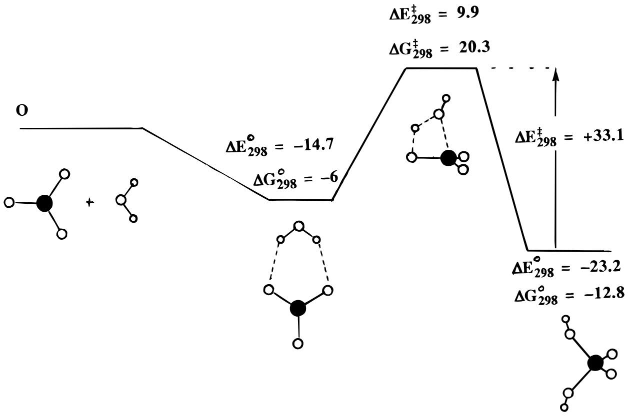

Figure 6. Energy diagram for the reaction $PO_3^- + H_2O \rightarrow (HO)_2PO_2^-$, giving internal energy changes, ΔE°, and free energy changes, ΔG°, and structures for reactants and transition state, obtained by the theoretical work of Wu and Houk.[10] All values are in kcal/mol.

The activation barrier for the reverse reaction, which corresponds to reaction 6, is predicted to be $\Delta E_6^\ddagger = 33.1$ kcal/mol. This value is much lower than the collision-induced threshold result, $\Delta E_6^\ddagger \approx 54$ kcal/mol.

The theoretical result may be too low; however, we doubt that the error could be as large as 20 kcal/mol. In general, one expects errors in the threshold determinations which are less than 5 kcal/mol. However, the threshold result may be less reliable when a very "tight" transition state is involved. A transition state where the free energy surface provides only a very narrow passage through the lowest energy pathway may lead to very low product intensities at the true, low-energy threshold and much higher intensities considerably above the threshold where the passage is much broader. Such a situation may lead to a threshold curve which has a long tail toward low energies. Examinations of several threshold curves obtained for the decomposition, eq 6, including that shown in Figure 5, did not provide direct evidence for the presence of such a tail. However, this does not necessarily exclude the existence of a tail of very low intensity. A very tight transition state should also lead to a large kinetic shift and the $\Delta E_6^\ddagger$ value corrected for the kinetic shift, i.e. $\Delta E_6^\ddagger$(c), should be much smaller than the CID values obtained with the fitting procedures (a) and (b), see eq 6. The results obtained show only a small decrease of the value in (c).

The vibrational frequencies for the transition state used for the kinetic shift evaluation (c) were the frequencies obtained by Wu and Houk.[10,14] Comparison[14] of the frequencies of the transition state with those of $(HO)_2PO_2^-$ shows that the two sets are very similar, particularly when the low frequencies, which make the important contributions, are compared. In other words, the vibrational frequencies do not correspond to a transition complex that is much tighter than the precursor ion and for this reason the evaluated $\Delta E_6^\ddagger$ with kinetic shift correction is small. The large discrepancy between the theoretical $\Delta E_6^\ddagger$ and the CID result indicates that in some cases, i.e. tight precursor ion and tight transition state, the actual reaction dynamics near the threshold may not be well described by the RRKM formalism and the use of normal frequencies, which underlie the fitting procedure used.

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(12) Chupka, W. A. *J. Chem. Phys.* **1959**, *30*, 191.

(13) Due to the limited time between collisional excitation of the precursor ion in Quadrupole Q_2 and detection in Q_3 (~30 μs in our apparatus), a certain extra amount of energy is required to speed up the decomposition near the threshold.

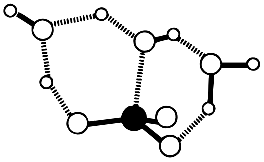
(14) The vibrational frequencies were not included in the Wu and Houk[10] publication. We are grateful to these authors for providing us with these data: $\bar{\nu}$ (cm^{-1}) $(HO)_2PO_2^-$, 222, 340, 352, 426, 472, 553, 554, 847, 875, 1156, 1170, 1179, 1410, 4125, 4126. Transition state: −1875 imaginary frequency set to zero in fitting procedure, 252, 287, 467, 499, 586, 645, 752, 887, 1035, 1275, 1409, 1556, 2099, 9112. Entropies S° at 298 K, in cal deg^{-1} mol^{-1}, $(HO)_2PO_2^-$ = 71.3; TS = 71.3.

(15) Ma, B.; Xie, Y.; Shen, M.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1993**, *115*, 1943.

(16) The estimates are based on assuming an ion molecule collision rate constant k_c of 10^{-9} molecules^{-1} cm^3 s^{-1} and the expression $k_c \exp(-\Delta G^\ddagger/RT)$ for the bimolecular rate constant. One-Torr H_2O pressures (i.e., 3×10^{16} molecules cm^{-3} and $T = 353$ K) were used for the ion lifetime estimates. Ion lifetimes should be less than 1 ms for equilibria to be observed in the apparatus.[6]

In any case, the present CID results are in agreement with the presence of a large energy barrier for the conversion of orthophosphate to metaphosphate, eq 6, as predicted by the theoretical work.[10]

(d) Insights Provided by the Theoretical Calculations and Conclusions. The theoretical results of Wu and Houk[10] for the conversion of $PO_3^-(H_2O)_n$, with $n = 1$ and 2, to orthophosphate hydrates, eq 7, are of special interest. These show that the activation energy barrier decreases somewhat with n. The lowest energy transition state structure obtained for the $n = 2$ is shown below (structure 12 in Wu and Houk[10]).



The structure illustrates clearly the assistance of the two additional water molecules which provide additional stabilization relative to the $n = 0$ transition state shown in Figure 6. The transition state energy $\Delta G_7^{\ddagger}(n = 2) \approx 18$ kcal/mol can be compared with $\Delta G_7^{\ddagger}(n = 0) \approx 20.3$ kcal/mol.

One can estimate[16] that at the average temperature, 80 °C, used in Keesee and Castleman's measurements,[6] only barriers less than 8 kcal/mol will lead to observable rates. On that basis, the theoretical results[10] predict that reaction 7 ($n = 2$) will be far too slow to lead to detectable changes. Because the $\Delta G^{\ddagger}$ for the reverse reaction 7, $\Delta G_7^{\ddagger}(n = 2)_{\text{rev}} \approx 32$ kcal/mol,[10] is very much higher due to the exothermicity of the forward reaction, its rates will be many orders of magnitude slower again which means that the observation of the equilibrium of reaction 7 is completely excluded. The latter prediction is in agreement with the present work where the formation of PO_3^- and hydrates from orthophosphate and hydrates was not observed—see orthophosphates hydration equilibria, section (b), and the very large barrier for the same process from CID measurements, section (c).

It is still of considerable interest to establish what occurred in the experiments.[6] Wu and Houk suggested that the thermodynamic data for the anomalous (2,3) hydration data[6] are due to an equilibrium, which does not involve the conversion to orthophosphate, eq 7, but the formation of hydrates $PO_3^-(H_2O)_3$ with several different structures. The most stable of these, see structure 6, ref 10, has one of the water molecules oriented so that its oxygen is pointing toward the phosphorus atom and is interacting with it. In fact, this structure is quite similar to the transition state, see structure above.[10] We feel that this proposal provides a good rationalization of the experimental[6] results. A similar explanation was also proposed in the theoretical work by Schaefer and co-workers.[15]

Finding the similarities between the most stable $PO_3^-(H_2O)_3$ (structure 6, ref 10) and the transition state structure very suggestive, an alternative explanation can also be considered. It is possible that orthophosphate hydrates were formed by reactive collisions of the $PO_3^-(H_2O)_n$, $n \leq 3$, with water molecules but without equilibrium being present, due to the occurrence of reaction 7 only in the forward direction. Although Wu and Houk predict a transition state for reaction 7 ($n = 2$) which is too high for the reaction to occur, the actual value might be somewhat lower and the crossings to the orthophosphate at higher n such as $n = 3$ might require even less energy. The forward reactions will be slow and incomplete and the absence of equilibrium might not have been noticed because the experimental technique[6] does not allow for independent changes of the time available for the reaction. Furthermore, once orthophosphates are formed, their hydration equilibria will be fast and superimpose themselves on the metaphosphate hydrates, introducing further complexity in the $(n-1,n)$ ion intensity ratios due to the inability of the mass spectrometer to distinguish between the $PO_3^-(H_2O)_n$ and $(HO)_2PO_2^-(H_2O)_{n-1}$ species.

Assuming that our proposal is correct, Keesee and Castleman's[6] data may still be the first gas phase experiments in which a conversion from meta to orthophosphate occurred and the Wu and Houk hydrate and transition state structures may be the first theoretical indications as to how such a conversion can occur. The proposal is also attractive because the metaphosphate ion is known to convert rapidly to orthophosphate in aqueous solution,[17] and gas phase experiments at high hydration numbers can be expected to approach the condensed phase results.

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[17] See discussion following: Jencks, W. P. *Brookhaven Symp. Biol.* **1962**, *15*, 134.