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Gas-Phase Ion Chemistry of HP_2^-, FP_2^-, and HP_2^+

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The gas-phase ion-molecule chemistry of the mass-selected ions HP_2^-, FP_2^-, and HP_2^+ has been studied in a tandem flowing afterglow selected-ion flow tube (FA-SIFT). Both HP_2^- and HP_2^+ are formed by direct electron impact on phosphine, followed by subsequent ion-phosphine reactions in the first flow tube. The related ion, FP_2^-, is formed via an ion-molecule reaction between HP_2^- and hexafluorobenzene. We have observed a number of reactions of HP_2^-, including hydride transfer and proton abstraction, as well as fluoride transfer and proton abstraction for FP_2^-. Using bracketing techniques, the gas-phase proton affinity of P_2 has been determined as 162 ± 3 kcal mol^{-1}, in good agreement with Nguyen and Fitzpatrick's theoretically predicted value of 158 ± 3 kcal mol^{-1}. The heats of formation of HP_2^-, HP_2^+, HPPH, FP_2^-, and FPPH have been estimated from the experimentally determined hydride, proton and fluoride affinities of P_2 and from the gas-phase acidities of HPPH and FPPH.

Introduction

Research into multiple bonding of heavier main group elements has continued unabated over the past decade.[1] Many such species have been isolated as stable compounds by utilizing bulky substituents which thwart oligomerization of the multiple bond. The phosphorus–phosphorus double bond is no exception, its species being some of the most studied of this class of compounds.[2] Studies of diphosphenes in solution have revealed details of electrophilic and nucleophilic attack on the double bond[3] as well as how they undergo electrochemical oxidation and reduction[4] and coordination to metal centers.[5]

The parent diphosphene, HPPH,[6–8] has attracted considerable theoretical interest[9a–n] since it was first detected as a thermal decomposition product of P_2H_4.[6] Three stable closed-shell structures have been found on the H_2P_2 potential energy surface using ab initio methods. They are (in decreasing relative order of stability)[9h,i] *trans*-HP=PH (0 kcal mol^{-1}), *cis*-HP=PH (+4 kcal mol^{-1}), and planar H_2PP (+30 kcal mol^{-1}). In addition, the open-shell singlet and triplet states of each of these isomers have been investigated.[9h,i] With the exception of triplet H_2PP (+27 kcal mol^{-1}), all open-shell states are higher in energy than the closed-shell structures. The barriers and transition states for isomerization between the cis and trans forms of HPPH via rotation and inversion have been considered by several authors,[9h,i] along with the barriers and transition states for the isomerization of H_2PP to HPPH.[9c,g–i] Various other ions, including HP_2^+,[9d,m] $H_2P_2^+$,[9a,j] $H_2P_2^{2+}$,[9d] $H_3P_2^+$,[9e,g] and $H_2P_2^-$,[9a,h] have also been considered.

The cis and trans forms of the related HPPX (X = F, Cl, OH, NH_2, CH_3, SiH_3) systems have also been studied computationally.[9m] The trans form is predicted to be 2–4 kcal mol^{-1} more stable than the cis form in all cases. When X = F, Cl, OH, and NH_2, the trans forms exhibit unusual bridged structures with HPP angles less than 90°. Since HP_2^+ also exhibits a bridged structure, close ion pair structures X^-PPH^+ have been proposed to explain these observations. We note, however, that other isomeric structures were not considered. For example several other stable isomers of formula H_2P_2O may exist, including H(HO)PP, HPP(O)H, H_2PPO, and cyclic HP(O)PH.

Research into the gas-phase ion chemistry of phosphine has revealed that both anions[10,11] and cations[11–14] related to diphosphenes can readily be formed by condensation reactions of various phosphorus ions with phosphine. Using an ICR mass spectrometer, Beauchamp and co-workers have shown that reaction between H_2P^- and PH_3 yields both $H_3P_2^-$ (eq 1) and HP_2^- (eq 2).[11] Both of these reactions are slow, with upper limits for the rate constant of 10^{-11} cm^3 molecule^{-1} s^{-1}. ICR,[11,12] drift,[13] and flowing afterglow studies[14] indicate that reactions between PH_3 and the ions P^+, PH^+, and PH_2^+ yield several new ions, including HP_2^+ (via eqs 3 and 4), $H_2P_2^+$, $H_3P_2^+$, and $H_4P_2^+$. These reactions are considerably faster than those shown in eqs 1 and 2. The ion–molecule reactions of such anions and cations have not been investigated until now.

$$H_2P^- + PH_3 \rightarrow H_3P_2^- + H_2 \tag{1}$$

$$H_2P^- + PH_3 \rightarrow HP_2^- + 2H_2 \tag{2}$$

$$P^+ + PH_3 \rightarrow HP_2^+ + H_2 \tag{3}$$

$$H_2P^+ + PH_3 \rightarrow HP_2^+ + 2H_2 \tag{4}$$

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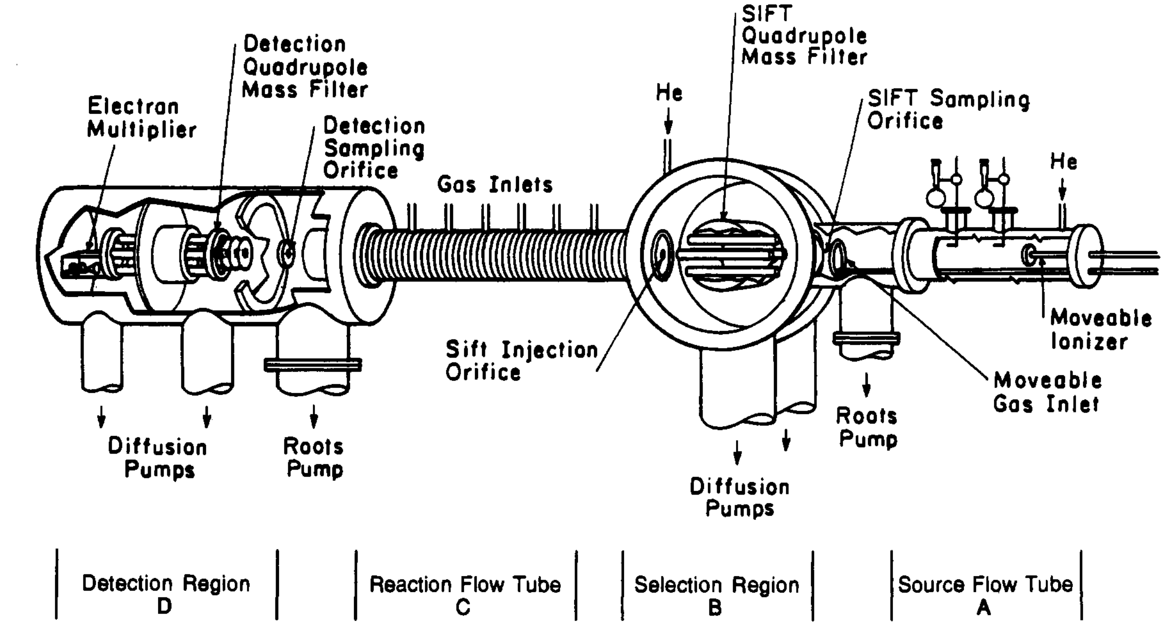

Figure 1. Schematic diagram of the FA-SIFT.

While studies on organosilicon species have revealed the fascinating chemistry of $HCSi^-$,[15] $CH_3SiCH_2^-$,[16] $CH_3Si(CH_2)_2^-$,[17] $HSiO^-$,[18] and CH_3OSiO^- and CH_3SiO^-,[19] the chemistry of analogous phosphorus species is less well defined.[20] As part of our ongoing research into the ion chemistry of novel organosilicon and organophosphorus species, we describe in this paper some of the gas-phase ion chemistry of HP_2^-, FP_2^-, and HP_2^+.

Experimental Section

All experiments were carried out at room temperature in a tandem flowing afterglow selected-ion flow tube (FA-SIFT) which has previously been described in detail.[21] A brief summary of the operation of this instrument is now given for those readers unfamiliar with the technique. The FA-SIFT is shown in Figure 1 and consists of four regions: a source flow tube for ion preparation (A), an ion selection and purification region (B), a second flow tube for studying the chemical reactions of the mass-selected ions (C) followed by the ion detection region (D).

Table I. Reactions of HP_2^- with Acids

reactant (AH)	$\Delta G_{acid}°$, kcal mol^{-1} [a]	A^- obsd?
CH_3NO_2	349.7 ± 2	no
$CF_3CF_2CH_2OH$	348.7 ± 6	clusters
$(CH_3)_3CSH$	346.3 ± 2	yes
H_2S	344.9 ± 2	yes
CH_3CO_2H	341.5 ± 2	yes

[a] Values taken from ref 22.

Ions are prepared in the source flow tube by electron impact on a suitable neutral precursor or by reactions between primary reagent ions (such as F^-, HO^-, and NH_2^-) and neutral reagents which are added further downstream. All ions are entrained in a rapidly flowing stream of helium buffer gas. At the end of the first flow tube, the helium and other neutrals are removed by pumping while the ions are sampled through a 2-mm orifice into the selection region where they are focused into a quadrupole mass filter via a series of electrostatic lenses. Tuning the quadrupole to only transmit ions of a certain m/z allows the ion of interest to be separated from all other ions. These mass-selected ions are injected into the second (reaction) flow tube, where they are entrained in a helium buffer gas. The ions undergo multiple collisions with the helium and are rapidly equilibrated to room temperature before being allowed to react with neutral reagents. All product ions are sampled into the detection region, where they are separated by a second quadrupole mass filter and counted with an electron multiplier.

Electron impact on phosphine in the source flow tube in either the negative or positive ionization modes gives a variety of condensation products $P_xH_y^{-/+}$ (where x = 1–3 and y = 0–6). Specifically, HP_2^- ions formed via electron impact on phosphine (0.03 Torr) were entrained in a stream of helium (0.3 Torr). When hexafluorobenzene was added downstream, several new ions were formed (eqs 5 and 6), including FP_2^-. These source conditions changed for the production of HP_2^+, where a lower pressure of phosphine (0.01 Torr) and a higher pressure of helium (0.45 Torr) were required to avoid reaction 7.[13]

$$HP_2^- + C_6F_6 \rightarrow FP_2^- + C_6F_5H \quad (5)$$

$$HP_2^- + C_6F_6 \rightarrow C_6F_5^- + FPPH \quad (6)$$

$$HP_2^+ + PH_3 \rightarrow H_4P^+ + P_2 \quad (7)$$

All reactions of HP_2^-, FP_2^-, and HP_2^+ were studied at 300 K at a helium buffer gas pressure of 0.5 Torr and a flow of 250 STP cm^3 s^{-1} in

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(25) The free energy of protonation may be converted to an enthalpy by estimating the entropy of protonation. See: Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2.
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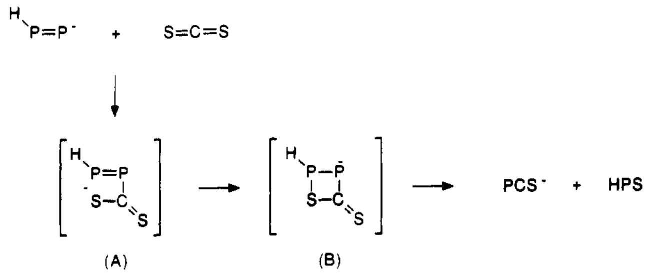
Scheme I



the reaction flow tube. Gases were obtained from commercial sources and were of the following purities: He, 99.995%; PH_3, 99.999%; CO_2, 99.5%; SO_2, 99.9%; COS, 97.7%; C_2H_2, 99.6%; H_2S, 99.5%; CH_3SH, 99.5%; F_4Si, 99.99%; $(CH_3)_3SiF$, >97%. All other reagents were obtained from commercial sources and were purified as necessary prior to use. The helium buffer gas was passed through a liquid-nitrogen-cooled molecular sieve trap before entering the flow tubes.

Since P_2, P_2H_2, and FP_2H are not available as neutrals, we must resort to bracketing techniques to determine hydride and fluoride affinities and gas-phase acidities. The major assumption of this technique is that gas-phase transfer of simple ions such as H^-, F^-, and H^+ occurs relatively rapidly if the reaction is exothermic. For simple species like those reported here, this assumption appears reasonable. In our bracketing experiments "no reaction" means that no decrease in reactant ion signal was observed within the time frame of the experiments. We are able to detect reactions which occur once in every 10 000 collisions.

Results and Discussion

A. Reactions of HP_2^-. The reactions of HP_2^- involving proton transfer are shown in Table I. Proton transfer to HP_2^- is likely to result in the formation of the thermodynamically favored HPPH, since ab initio calculations indicate that this species is more stable than H_2PP by some 27 kcal mol^{-1}.[9h,i] Our estimates of the heat of formation of HP_2^- and HPPH, as derived from these and other experimental measurements, are discussed later in the thermochemistry section.

We have also studied the reactions of HP_2^- with a number of other reagents. Hydride transfer from HP_2^- to CO_2 (eq 8), CS_2 (eq 9), and SO_2 (eq 11) is observed. A second reaction pathway between HP_2^- and CS_2 results in the formation of PCS^- (eq 10). We propose the mechanism shown in Scheme I for this reaction, in analogy to the reaction of CH_2N^- with COS.[32]

$$HP_2^- + CO_2 \rightarrow HCO_2^- + P_2 \tag{8}$$

$$HP_2^- + CS_2 \rightarrow HCS_2^- + P_2 \tag{9}$$

$$HP_2^- + CS_2 \rightarrow PCS^- + HPS \tag{10}$$

$$HP_2^- + SO_2 \rightarrow HSO_2^- + P_2 \tag{11}$$

$$HP_2^- + SO_2 \rightarrow HP_2O^- + SO \tag{12}$$

In addition, HP_2^- reacts with SO_2 by a second pathway, involving oxygen atom abstraction, which results in the formation of the oxyanion HP_2O^- (eq 12). Similarly, sulfur atom abstraction from COS is exclusively observed, yielding HP_2S^- (eq 13). Both of these classes of reactions have been previously observed with other ions.[18,31]

$$HP_2^- + COS \rightarrow HP_2S^- + CO \tag{13}$$

Scheme II

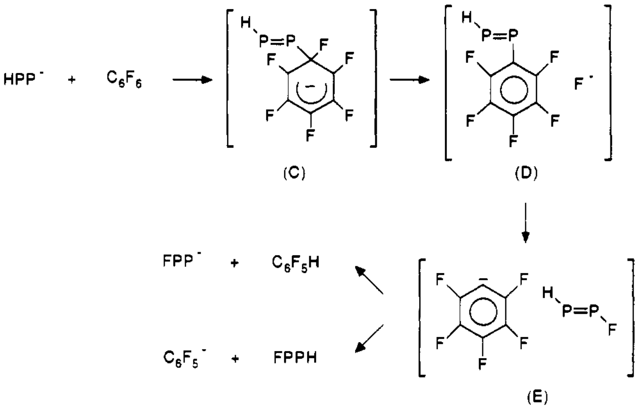
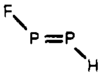
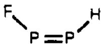
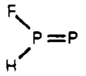


Table II. Reactions of FP_2^-

reactant	fluoride ion affinity, kcal mol^{-1} [a]	$\Delta G_{acid}°$, kcal mol^{-1} [b]	F^- transfer obsd?	deprotonation obsd?
SiF_4	60.0		yes	
HCO_2H	45.3	338.2	yes	yes
CH_3CO_2H	44.1	341.5	yes	yes
$(CH_3)_3SiF$	38.2	unknown	yes	no
H_2S	34.6	344.9	yes	yes
CH_3SH	34.2	350.6	no	no
$CH_3(CH_2)_3OH$	32.2	368.8	no	no
COS	31.8		no	
CS_2	31.3		no	

[a] Values taken from ref 26. Errors are ±2.5 kcal mol^{-1}. [b] Values taken from ref 22. Errors are ±2.0 kcal mol^{-1}.

Table III. Calculated Geometries and Energies for $[H,F,P_2]$ Isomers at the 6-31G** Level

isomer	geometry[a]		energies abs, hartrees	energies rel, kcal mol^{-1} [b]
	F–P	1.595	−781.450 230	0
	P–P	1.994		
	P–H	1.409		
	F–P–H	103.6		
	P–P–H	89.7		
	F–P	1.595	−781.446 709	+2.2
	P–P	1.999		
	P–H	1.407		
	F–P–H	106.6		
	P–P–H	97.6		
	F–P	1.578	−781.412 017	+24.0
	P–P	1.891		
	P–H	1.382		
	F–P–H	129.1		
	P–P–H	132.2		

[a] distances in angstroms and angles in degrees. [b] $E_{rel} = E_X - E_{trans}$.

Hexafluorobenzene has proved to be a useful reagent in the study of gas-phase ion–molecule reactions due to its high reactivity toward nucleophiles.[18,33] It reacts with HP_2^- to form the two products shown in eqs 5 and 6. Both of these reactions are exothermic. We envisage these reactions as proceeding via the intermediates C–E, as shown in Scheme II. Thus initial nucleophilic attack on the benzene ring forms the Meisenheimer complex C, which can lose F^- to form the ion–molecule complex D. Nucleophilic fluoride ion attack on phosphorus results in a second ion–molecule complex E, from which both of the observed products could arise either by dissociation (eq 5) or by proton transfer (eq 6).

Finally, HP_2^- reacts with CH_3SSCH_3 via nucleophilic attack on sulfur,[34] forming the ion–molecule complex $[CH_3S^-(HPPSCH_3)]$. Dissociation of this complex leads to the products shown in eq 14, while proton transfer yields the products shown in eq 15.

$$HP_2^- + CH_3SSCH_3 \rightarrow CH_3S^- + HP_2SCH_3 \tag{14}$$

$$HP_2^- + CH_3SSCH_3 \rightarrow CH_3SP_2^- + CH_3SH \tag{15}$$

B. Reactions of FP_2^-. The reactions of FP_2^- with various neutrals as well as the gas-phase acidities and fluoride ion affinities of those neutrals are given in Table II. This ion reacts only by proton abstraction and fluoride ion transfer, in contrast to the reactions HP_2^- described above. We have carried out ab initio

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Table IV. Reactions of HP_2^+

reactant	proton affinity, kcal mol^{-1} [a]	products[b]
H_2S	170.2	$H_3S^+ + P_2$
H_2O	166.5	$H_3O^+ + P_2$
SO_2	161.6	$HSO_2^+ + P_2$ $PO^+ + HPSO$
$(CF_3)_2CO$	161.5	no reaction
HCCH	153.3	m/z 77[c] $[H_3C_2P_2]^{+}$[c]
COS	151.0	$HP_2S^+ + CO$

[a] Values taken from ref 27. Errors are ±2.0 kcal mol^{-1} or better. [b] Neutral products are inferred. [c] Structure of ion is unknown.

calculations[35] on three possible singlet isomers, viz. the cis and trans forms of FPPH and planar FHPP, in order to ascertain the most stable form of $[F,H,P_2]$. The results are shown in Table III. Interestingly, the relative energies of the various $[F,H,P_2]$ isomers parallel those of H_2P_2:[9h,i] *trans*-FPPH, 0 kcal mol^{-1}; *cis*-FPPH, +2.2 kcal mol^{-1}; planar FHPP, +24.0 kcal mol^{-1}. Thus proton transfer to FP_2^- is likely to result in the formation of the thermodynamically favored product FPPH.

C. Reactions of HP_2^+. The gas-phase chemistry of phosphorus cations is of fundamental interest with regard to interstellar chemistry[36] as well as to the atmospheric chemistry of the Jovian planets.[37] The results of our preliminary studies of the reactions of HP_2^+ with a number of neutral reagents are shown in Table IV. A minor amount of sulfur atom abstraction is observed at high pressures of COS. HP_2^+ reacts with SO_2 to form both HSO_2^+ and PO^+. When acetylene is used as the reagent gas, product ions with mass to charge ratios of 77 and 89 are observed. The latter corresponds to an adduct whose structure is unknown. Similarly, the identity of the m/z 77 ion is unknown. We plan to examine this reaction and other reactions of HP_2^+ in further detail and will report our findings in due course.

D. Thermochemistry. (i) Heats of Formation of HP_2^- and HPPH. One of the reactions observed for HP_2^- is that of hydride transfer. Thus the hydride affinity of P_2, as defined by eq 16, can be bracketed by allowing HP_2^- to react with a series of compounds of known hydride affinity (HA).[24] We have found that HP_2^- will not hydride-transfer to acetone (HA = 39.6 kcal mol^{-1}) or benzaldehyde (HA = 45.9 kcal mol^{-1}) and only very slowly hydride-transfers to CO_2 (HA = 51.6 kcal mol^{-1}). Hydride transfer to SO_2 (HA = 63.0 kcal mol^{-1}) and CS_2 (HA = 67.3 kcal mol^{-1}) is observed. Since hydride transfer to CO_2 is qualitatively slower than H^- transfer to SO_2 and CS_2, we have assigned a value of 51 ± 5 kcal mol^{-1} to the hydride affinity of P_2. Given that the gas-phase heats of formation of H^- and P_2 are known,[22,23] the heat of formation of HP_2^- can be calculated via eq 17. Therefore we estimate the heat of formation of HP_2^- to be 18 ± 5 kcal mol^{-1}. It is also possible to bracket the gas-phase basicity of HP_2^- (eq 18) and as a result determine the heat of formation of the parent neutral HPPH. Examination of Table I reveals that proton abstraction from acetic acid, H_2S, and *tert*-butyl mercaptan is observed, while HP_2^- gives only clusters with $CF_3CF_2CH_2OH$ and fails to deprotonate nitromethane. Thus, from the upper and lower limits of proton transfer, the gas-phase basicity of HP_2^- is estimated to be $\Delta G_{acid}° = 348 \pm 3$ kcal mol^{-1}. Taking the gas-phase basicity and heat of formation of HP_2^-, the heat of formation of HPPH can be estimated via eq 19.[25] The value obtained this way, $\Delta H_f°(HPPH) = 29 \pm 7$ kcal mol^{-1}, compares reasonably well with Fehlner and Callen's value of 26 ± 8 kcal mol^{-1}, derived from positive-ion appearance potential measurements.[7]

$$HP_2^- \xrightarrow{HA(P_2)} H^- + P_2 \qquad (16)$$

$$\Delta H_f°(HP_2^-) = \Delta H_f°(P_2) + \Delta H_f°(H^-) - HA(P_2) \qquad (17)$$

$$HPPH \xrightarrow{\Delta G_{acid}°} HP_2^- + H^+ \qquad (18)$$

$$\Delta H_f°(HPPH) = \Delta H_f°(HP_2^-) + \Delta H_f°(H^+) - \Delta H_{acid}°(HPPH) \qquad (19)$$

(ii) Heats of Formation of FP_2^- and FPPH. The heat of formation of FP_2^- can be determined from its fluoride ion affinity (FIA) as shown in eq 20.[26] Table II indicates that FP_2^- does not fluoride-transfer to CS_2, COS, *n*-BuOH, and MeSH. Fluoride ion transfer is observed between FP_2^- and H_2S, Me_3SiF, acetic acid, formic acid, and silicon tetrafluoride. On the basis of an upper limit for fluoride ion transfer to H_2S and a lower limit for no F^- transfer to MeSH, we estimate the fluoride ion affinity of P_2 to be 34 ± 3 kcal mol^{-1}. Using eq 10, $\Delta H_f°(FP_2^-)$ is determined to be −59 ± 4 kcal mol^{-1}.

$$FP_2^- \xrightarrow{FIA(P_2)} F^- + P_2 \qquad (20)$$

$$\Delta H_f°(FP_2^-) = \Delta H_f°(P_2) + \Delta H_f°(F^-) - FIA(P_2) \qquad (21)$$

In a manner analogous to that described above for HPPH, we have allowed FP_2^- to react with a number of acids. The results of this study are shown in Table II. Thus FP_2^- deprotonates formic acid, acetic acid, and H_2S but does not deprotonate MeSH and *n*-BuOH. On the basis of the upper and lower limits of proton transfer, we estimate the gas-phase basicity of FP_2^- to be $\Delta G_{acid}° = 348 \pm 4$ kcal mol^{-1}. Taking the gas-phase basicity and heat of formation of FP_2^-, the heat of formation of FPPH is estimated to be −48 ± 7 kcal mol^{-1} via eq 22.[25] Surprisingly, the gas-phase basicities of FP_2^- and HP_2^- are essentially the same, within experimental error.

$$\Delta H_f°(FPPH) = \Delta H_f°(FP_2^-) + \Delta H_f°(H^+) - \Delta H_{acid}°(FPPH) \qquad (22)$$

(iii) Heat of Formation of HP_2^+. By allowing HP_2^+ to react with various gas-phase bases of known proton affinity (PA), we have bracketed the gas-phase proton affinity of P_2 (eq 23).[27] Table IV shows that HP_2^+ proton-transfers to H_2S and H_2O, but only very slowly to SO_2. No proton transfer occurs with hexafluoroacetone, acetylene, and COS. Therefore we estimate the proton affinity of P_2 to be 162 ± 3 kcal mol^{-1}. This value compares well with the theoretically predicted value of 158 ± 3 kcal mol^{-1} determined by Nguyen and Fitzpatrick.[9d] We estimate $\Delta H_f°(HP_2^+) = 238 \pm 4$ kcal mol^{-1} via eq 24.

$$HP_2^+ \xrightarrow{PA(P_2)} H^+ + P_2 \qquad (23)$$

$$\Delta H_f°(HP_2^+) = \Delta H_f°(P_2) + \Delta H_f°(H^+) - PA(P_2) \qquad (24)$$

This value does not compare well with those of Fehlner and Callen [$\Delta H_f°(HP_2^+) = 289 \pm 8$ kcal mol^{-1}],[7] Saalfeld and Svec [$\Delta H_f°(HP_2^+) = 267 \pm 7$ kcal mol^{-1}],[28a] and Wada and Kiser [$\Delta H_f°(HP_2^+) = 257 \pm 9$ kcal mol^{-1}],[28b] all of which were determined via appearance potential measurements. These previously determined heats of formation of HP_2^+, when combined with those of P_2 and H^+, predict proton affinities of P_2 to be 111, 133, and 143 kcal mol^{-1}, respectively. These values are clearly at odds with both our experimentally determined value and the theoretically predicted value.[9d]

(iv) Enthalpies of Reactions Shown in Eqs 2–6. Previous workers have commented on the lack of reliable thermochemical data for phosphorus species.[11,12] We note that the heats of formation of simple ionic phosphorus species hinge on accurate values for the heats of formation of the parent neutrals. Our estimated heats of formation of HP_2^-, HP_2^+, HPPH, FP_2^-, and FPPH, together with the best thermochemical data available on various other relevant species, are summarized in Table V. By combining the appropriate thermochemical values, the enthalpies of the reactions shown in eqs 2–6 have been estimated (the experimental errors are ±8 kcal mol^{-1}). Reactions 3–6 are exothermic by 80, 24, 41, and 28 kcal mol^{-1}, respectively, while the slow reaction between

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Table V. Heats of Formation of Reactant and Product Species

species	$\Delta H_f^\circ{}_{298}$, kcal mol^{-1}	ref	species	$\Delta H_f^\circ{}_{298}$, kcal mol^{-1}	ref
H^+	365.7 ± 0.1	22	HP_2^+	238 ± 4	this work
H^-	34.7 ± 0.1	22	HP_2^-	18 ± 5	this work
H_2	0	23a	FP_2^-	−59 ± 4	this work
F^-	−59.5 ± 0.5	22	HPPH	29 ± 7	this work
P^+	317.0 ± 0.2	22	FPPH	−48 ± 7	this work
PH_2^+	261.0 ± 0.6	22	$C_6F_5^-$	−190.5 ± 8.0	22
PH_2^-	6.5 ± 2.4	22	C_6F_5H	−192.6 ± 1.6	23b
PH_3	1.3 ± 0.4	29	C_6F_6	−228.3 ± 0.3	23b
P_2	34.3 ± 0.5	23a			

H_2P^- and PH_3 to yield HP_2^- (eq 2) is endothermic by 10 kcal mol^{-1}. The reaction shown in eq 2 is therefore likely to be an example of an "entropy-driven" reaction.[30] The typical gain in entropy for a reaction between two reactants resulting in the formation of three products is of the order of 20 cal K^{-1} mol^{-1}. Thus, $T\Delta S$ is generally about 6 kcal mol^{-1}. Considering the experimental uncertainty of the enthalpy of this reaction, it comes as no surprise that it occurs.

E. Comparisons between Phosphorus and Nitrogen Ions. DePuy and co-workers have compared the reactions of H_2P^- and H_2N^-.[38] They found that the reactions of H_2P^- are often qualitatively similar to those of H_2N^-. The observed differences were attributed to the weaker nucleophilicity of H_2P^-.

To date, there has been no experimental evidence for the existence of HN_2^- in the gas phase. Bowie et al. have noted that the thiomethoxide ion does not hydride-transfer to N_2 in an ICR mass spectrometer.[39] This results in an upper limit of HA(N_2) < 25.4 kcal mol^{-1}.[24] Since high-level ab initio calculations have not been carried out on HN_2^-, we cannot turn to theory as a guide as to whether this species is stable or whether it spontaneously loses an electron to form the radical species $HN_2^\bullet$[40] or a hydride ion to form N_2. Clearly, N_2 is much less willing than P_2 to accept the hydride at the expense of a π bond. N_2 (PA = 118.2 kcal mol^{-1})[27] is also a weaker gas-phase base than P_2 (PA = 162 kcal mol^{-1}), for similar reasons. An analogous situation arises for the pair CO (HA = 8 kcal mol^{-1},[24] PA = 141.9 kcal mol^{-1}[27]) and SiO (HA = 49 kcal mol^{-1},[18] PA = 189.3 kcal mol^{-1}[41]). Both of these examples indicate the weaker π bonding of third-row atoms relative to their second-row analogues.

Conclusions

In summary, we have shown that electron impact on phosphine in a FA-SIFT results in the condensation products $P_xH_y^{-/+}$ (where x = 1–3 and y = 0–6). FP_2^- is formed in the first flow tube via an ion–molecule reaction between HP_2^- and hexafluorobenzene. Using the mass selection capabilities of the FA-SIFT, we have studied the gas-phase ion–molecule chemistry of HP_2^-, FP_2^-, and HP_2^+. HP_2^- reacts via a number of pathways, including hydride transfer and oxygen and sulfur atom abstraction. Using bracketing techniques, we have determined the hydride affinity, fluoride ion affinity, and proton affinity of P_2. They are 51 ± 5, 34 ± 3, and 162 ± 3 kcal mol^{-1}, respectively. In addition we have estimated the gas-phase acidities of HPPH (ΔG_{acid}° = 348 ± 3 kcal mol^{-1}) and FPPH (ΔG_{acid}° = 348 ± 4 kcal mol^{-1}). Using these values, we have estimated the heats of formation of HP_2^-, HP_2^+, HPPH, FP_2^-, and FPPH.

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^{113}Cd Shielding Tensors of Cadmium Compounds. 8. Solid-State ^{113}Cd NMR Studies of Poly(bis(glycine)cadmium chloride)

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The ^{113}Cd shielding tensor of the cadmium compound poly(bis(glycine)cadmium chloride) has been determined via powder and single-crystal solid-state NMR experiments. The isotropic chemical shift determined was 115 ppm, and the individual shielding tensor components obtained through single crystal methods are σ_{11} = 263.0 ± 0.4 ppm, σ_{22} = 196.0 ± 2.0 ppm, and σ_{33} = −111.0 ± 3.6 ppm. The spatial arrangement of the molecules in the crystal lattice generates two magnetically distinguishable tensors. The coordination about the cadmium metal ion is a distorted octahedron and can be described in terms of three molecular planes. By the use of these planes, the ligand contribution to the ^{113}Cd nuclear shielding could be predicted by the progression in the direction of lower shielding of the best least-squares planes of atoms: O–O–O–Cl > O–O–Cl–Cl > O–Cl–Cl–Cl. Here O represents a carboxylate oxygen from glycine and Cl a chloride ion. Generally, chlorides are more deshielding ligands of cadmium than are carboxylate oxygens. On the basis of this assessment and a collection of single-crystal experimental observations on cadmium compounds, an assignment of the ^{113}Cd shielding tensor to the appropriate lattice site was accomplished. The most shielded tensor element, σ_{33}, is oriented nearly perpendicular to the most shielding best least-squares plane defined by three oxygens and one chloride. The most deshielding tensor element is aligned mostly perpendicular to the most deshielding best least-square plane defined by three chlorides and one oxygen. The σ_{22} component is most perpendicular to the plane defined by two chlorides and two oxygens.

Introduction

Studies of NMR chemical-shifts by solid-state NMR provide more information about the electronic shielding of a nucleus than the corresponding liquid-state isotropic chemical shifts. The use of static or magic-angle-spinning (MAS) methods on powder samples yields the principal elements of the shielding tensor (i.e. σ_{xx}, σ_{yy}, and σ_{zz}). NMR experiments of oriented single crystals yield, in addition to the principal elements of the shielding tensor, the direction of the shielding tensor in the molecular frame. Because of fast molecular tumbling, most chemical shifts determined in the liquid state represent only an average of the shielding

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