

Gas-Phase Chemistry of H_2P^-

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Abstract: The gas-phase ion-molecule chemistry of H_2P^- has been investigated by using the flowing afterglow technique. Generated by proton abstraction from PH_3 by H_2N^- or HO^- , H_2P^- reacts with N_2O , CO_2 , OCS , CS_2 , O_2 , NO_2 , SO_2 , CH_3X , and $(\text{CH}_3)_3\text{SiCl}$ to yield a variety of ion products. Products usually arise from initial nucleophilic attack of H_2P^- on the neutral, followed by intramolecular proton transfer and/or expulsion of a neutral fragment. Many of the reactions are similar to those for H_2N^- , though differences are attributable to the weaker nucleophilicity of H_2P^- . Product branching ratios and reaction rate constants are reported, and possible mechanistic pathways are discussed.

The gas-phase negative ion chemistry of phosphine has not been thoroughly investigated. Using ion cyclotron resonance spectroscopy, Beauchamp and co-workers¹⁻³ have bracketed the gas-phase acidity of phosphine and Brauman et al.⁴ have ordered the relative acidities of a number of binary hydrides. In doing so they have studied the simplest ion-molecule reactions of H_2P^- , those involving proton transfer. However Beauchamp notes that the observation of negative ions with the ICR spectrometer is more difficult than the observation of positive ions; the cross section for electron capture is smaller by orders of magnitude than that for ionization. Direct electron impact on phosphine is not a convenient source for H_2P^- since it also produces HP^- , P^- , and H^- .^{1,5} This limitation can be overcome^{1,4} by starting with an initial species that provides a high yield of one negative ion by electron impact and that, by subsequent proton transfer from phosphine, gives the desired phosphide anion.

In the present work the ability to carry out sequential ion-molecule reactions in a flowing afterglow apparatus is employed first to generate high yields of H_2P^- and then to examine subsequent ion-molecule reactions between H_2P^- and neutral reactants. Electron impact on ammonia produces H_2N^- ; rapid, complete reaction with phosphine gives H_2P^- ; introduction of other neutral reagents further downstream allows the study of ion-molecule reactions of phosphide. Beauchamp¹ demonstrated that H_2P^- reacts very slowly with PH_3 to give $\text{HP}_2^- + 2\text{H}_2$ and $\text{H}_3\text{P}_2^- + \text{H}_2$; with the exception of this study and those of proton-transfer reactions the present publication is the first report of gas-phase ion-molecule reactions of phosphide with other molecules.

We wish to report here that phosphide reacts with a series of molecules (N_2O , CO_2 , OCS , CS_2 , O_2 , NO_2 , SO_2 , CH_3X , and $(\text{CH}_3)_3\text{SiCl}$) to give a variety of ion products. Some of these anions were expected in analogy with the reactions of amide,⁶ but others are generated by completely unprecedented processes. Some of the species are known, but most interestingly a whole series of heretofore unknown ions has been generated. Reactions of H_2P^- proceed with rate constants that are generally slower than the corresponding H_2N^- reaction rate constants.

We describe here the reactions of H_2P^- with the neutrals listed above, the products formed, the branching ratios for the various products, and the overall reaction rate constants. These results are compared to those for the reactions of amide,⁶ and the mechanistic pathways for the H_2P^- reactions are discussed.

Experimental Section

These experiments were performed at 298 K in a flowing afterglow system which has been described previously.⁷ H_2N^- was generated by

(1) Holtz, D.; Beauchamp, J. L.; Eyley, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 7045.

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(3) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1433.

(4) Brauman, J. I.; Eyley, J. R.; Blair, L. K.; White, M. J.; Comisarow, M. B.; Smyth, K. C. *J. Am. Chem. Soc.* **1971**, *93*, 6360.

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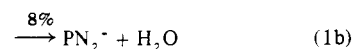
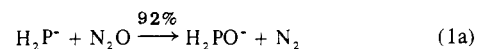
(6) Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H., manuscript in preparation.

electron impact on ammonia and H_2P^- was formed by the rapid proton abstraction reaction of amide with phosphine. Hydroxide was formed by dissociative electron attachment to nitrous oxide followed by rapid hydrogen atom abstraction from methane. Typical helium pressures and flow rates range from 0.3 to 0.5 torr and 140 to 240 STP $\text{cm}^3 \text{s}^{-1}$, respectively. Neutral reactant flow rates were determined by monitoring the pressure increase with time in a calibrated volume. Rate constants were measured by following reactant ion counts as a function of reaction time.

All gases were obtained from commercial suppliers and were of the following purities: He (99.995%), NH_3 (99.999%), N_2O (99.99%), CH_4 (99.99%), CO_2 (99.8%), OCS (97.5%), O_2 (99.99%), SO_2 (99.9%), NO_2 (99.9%), CH_3Cl (99.5%). The liquids CS_2 , CH_3Br , CH_3I , and $(\text{C}-\text{H}_3)_3\text{SiCl}$ were distilled before use.

Results

The reaction between phosphide and nitrous oxide will serve to typify the means by which results are obtained. Amide ion, H_2N^- , is generated by adding ammonia near the electron gun 135 cm upstream from the detector. Since water is extremely difficult to eliminate from the system, we usually observe about 10% hydroxide ion impurity. Subsequent introduction of a very small flow (≤ 0.05 STP $\text{cm}^3 \text{s}^{-1}$) of phosphine through an inlet positioned 105 cm upstream from the detector results in quantitative conversion to H_2P^- . Although a mixture of H_2N^- and HO^- is initially present, no complications arise in the production of H_2P^- since both are strong gas-phase bases and react with phosphine at the gas kinetic rate. Also, although reactions do occur between H_2P^- and PH_3 to give $\text{HP}_2^- + 2\text{H}_2$ and $\text{H}_3\text{P}_2^- + \text{H}_2$, the small rate constants for these processes ($< 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and the low flows of PH_3 in our system prevent significant occurrence, and the only observable anion in the mass spectrum is H_2P^- . Addition of N_2O at least 35 cm further downstream generates two product ions, one at m/z 49 and one at m/z 59, which we identify as H_2PO^- and PN_2^- , respectively.



To measure the relative yields of the two products, N_2O is introduced and the ion signals for H_2P^- , H_2PO^- , and PN_2^- are monitored as the flow of N_2O is varied from 0 to ~ 1 STP $\text{cm}^3 \text{s}^{-1}$. After normalization of the total ion signal, a plot of the relative intensity of a product ion (I_p) vs. the relative conversion of H_2P^- (ΔI_{33}) gives a straight line (Figure 1), the slope of which is equal to the branching ratio for that product. Thus $\text{H}_2\text{P}^- + \text{N}_2\text{O}$ gives 92% H_2PO^- (eq 1a) and 8% PN_2^- (eq 1b). The neutral reagents, product ions, and branching ratios for all the H_2P^- reactions studied are given in Table I. Also included for comparison are data for the analogous reactions of H_2N^- . Discrimination of the quadrupole mass filter against higher mass ions was minimized by adjusting the resolution until no further change was observed

(7) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H.; Stewart, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4229.

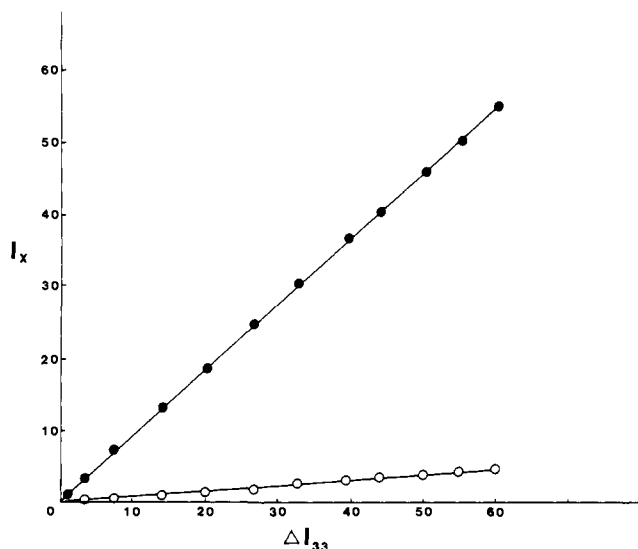


Figure 1. Relative intensity of product ion (I_x) vs. percent conversion of reactant H_2P^- (ΔI_{33}) for the reaction of H_2P^- with N_2O : (●), H_2PO^- ; (○), PN_2^- . Slope of line for $H_2PO^- = 0.92$ and slope of line for $PN_2^- = 0.08$ (0.3 torr He, 298 K).

Table I. Products and Branching Ratios for the Reactions of H_2P^- and H_2N^-

neutral	products ^a (branching ratio) ^b	
	H_2P^-	H_2N^- ^c
N_2O	$PN_2^- + H_2O$ (0.08) $H_2PO^- + N_2$ (0.92)	$N_3^- + H_2O$ (0.72) — $HO^- + HN_3$ (0.28)
CO_2	$H_2PCO_2^-$ (1.00)	— $NCO^- + H_2O$ (1.00)
OCS	$H_2PS^- + CO$ (0.89) $PCO^- + H_2S$ (0.09)	$H_2NS^- + CO$ (0.52) $NCO^- + H_2S$ (0.06) $HS^- + HNCO$ (0.42)
	H_2PCOS^- (0.02)	—
CS_2	$PCS^- + H_2S$ (0.60) $H_2PCS_2^-$ (0.11) $PS^- + H_2CS$ (0.29) $\xrightarrow{CS_2} PS_2^- + CS$	$NCS^- + H_2S$ (0.54) $HS^- + HNCS$ (0.46)
O_2	$PO_2^- + H_2$ (1.00)	— $HO^- + HNO$ ^d
NO_2	$NO_2^- + H_2P$ (1.00)	$NO_2^- + H_2N$ (1.00) ^e
SO_2	$SO_2^- + H_2P$ (0.32) $PSO^- + H_2O$ (0.05) $PO_2^- + H_2S$ (0.22) $H_2PSO_2^-$ (0.40)	$SO_2^- + H_2N$ (0.66) $NSO^- + H_2O$ (0.26) $HO^- + HNSO$ (0.08)
CH_3Cl	$Cl^- + H_2PCH_3$ (1.00)	$Cl^- + H_2NCH_3$ ^f $CH_2Cl^- + NH_3$
CH_3Br	$Br^- + H_2PCH_3$ (1.00)	$Br^- + H_2NCH_3$ ^f $CH_2Br^- + NH_3$
CH_3I	$I^- + H_2PCH_3$ (1.00)	$I^- + H_2NCH_3$ $CH_2I^- + NH_3$
$(CH_3)_3SiCl$	$Cl^- + H_2PSi(CH_3)_3$ (1.00)	$Cl^- + H_2NSi(CH_3)_3$ (1.00) ^g

^a Identity of neutral products is assumed. ^b Product distributions were measured under conditions where mass discrimination is minimized (see text). Where adduct is formed the values will be dependent on helium pressure. ^c Reference 6 unless otherwise noted. ^d Reference 29. ^e Reference 30. ^f Reference 31. ^g Reference 32.

in the ratio of a high mass ion to a low mass ion. In each branching ratio measurement the sum of the total ion intensities was equal, within experimental error ($\pm 20\%$), to the initial reactant ion intensity.

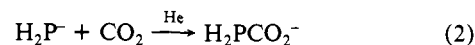
Table II. Rate Constants and Efficiencies for the Reactions of H_2P^- and H_2N^-

	H_2P^-		H_2N^-		
	neutral	k_{exptl}^a , $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	efficiency ^b	efficiency ^b	ref
N_2O		2.3×10^{-12}	0.002	0.24	6
CO_2^c		$<1 \times 10^{-12}$	<0.001	0.84	6
OCS		3.2×10^{-11}	0.023	1.0	6
CS_2		1.4×10^{-10}	0.096	0.97	6
O_2		1.5×10^{-12}	0.002	0.04	29
NO_2		1.3×10^{-9}	~1	~1	30
SO_2		2.9×10^{-11}	0.018	1.4	6
CH_3Cl		1.1×10^{-10}	0.056	0.63	31
CH_3Br		8.2×10^{-10}	0.47	0.48	31
CH_3I		1.3×10^{-9}	0.77	1.3	6
$(CH_3)_3SiCl$		1.8×10^{-9}	~1	~1	32

^a Average of three or four determinations; experimental precision, $\pm 10\%$; total estimated error, $\pm 25\%$. ^b Efficiency = $k_{\text{exptl}}/k_{\text{ADO}}$. k_{ADO} calculated by the method of Su and Bowers.²⁸ ^c Only one measurement of the reaction rate constant for $H_2P^- + CO_2$ was made; see text.

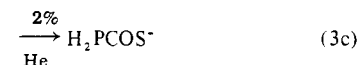
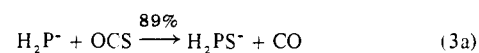
Absolute rate constants are measured by using the established flowing afterglow kinetic method.⁷ A measured flow of N_2O is introduced through the moveable inlet and the disappearance of the H_2P^- ion signal is followed as the reaction distance is varied. The rate constants were measured at several neutral flow rates and helium pressures, and the reported rate constants are averages of three or four determinations. For the reaction $H_2P^- + N_2O$ the overall rate constant is $k = 2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Rate constants for all reactions studied, as well as the reaction efficiencies, $k_{\text{exptl}}/k_{\text{ADO}}$, are given in Table II. The efficiency data from the corresponding H_2N^- reactions are included for comparison. The experimental precision of each rate constant is $\pm 10\%$. Calibration of the instrument against the known rate constant for the reaction $He^+ + N_2$ gave $1.2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (standard deviation 13%, an average of five determinations), in exact agreement with that reported.⁷ Rate constants are estimated to be accurate to $\pm 25\%$.

Phosphide reacts with carbon dioxide to form only the adduct $H_2PCO_2^-$ (eq 2), which can be thought of as a phosphorus analogue of the bicarbonate ion. This reaction is extremely inefficient.



As a consequence we were not able to measure the rate constant at various neutral flows and helium pressures; in order to observe any fall off in the H_2P^- signal, it was necessary to conduct the experiment at the maximum measurable flow of CO_2 and at 0.5 torr helium. The resulting rate constant $<1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ should be considered an upper limit at these conditions. Since adduct formation usually requires collisional stabilization, this rate constant is expected to depend on helium pressure.

The reaction with carbonyl sulfide (eq 3) is much more facile.



Besides adduct formation, H_2PS^- , the anion of phosphinothious acid, and PCO^- , phosphinidyne methoxide, are also formed. Since H_2P^- and HS^- have the same mass-to-charge ratio, we cannot distinguish whether the conjugate acid-base pair $HS^- + HPCO$ is formed in addition to $PCO^- + H_2S$, as in the corresponding amide reactions. Evidence that some HS^- is formed is found in the observation that the kinetic plots exhibit some upward curvature at the higher conversions of H_2P^- ; that is, at higher conversions the apparent I_{33} does not fall off as rapidly as it should due to loss of H_2P^- , indicating the formation of another ion at m/z 33, namely, HS^- . Nonetheless, when this is taken into ac-

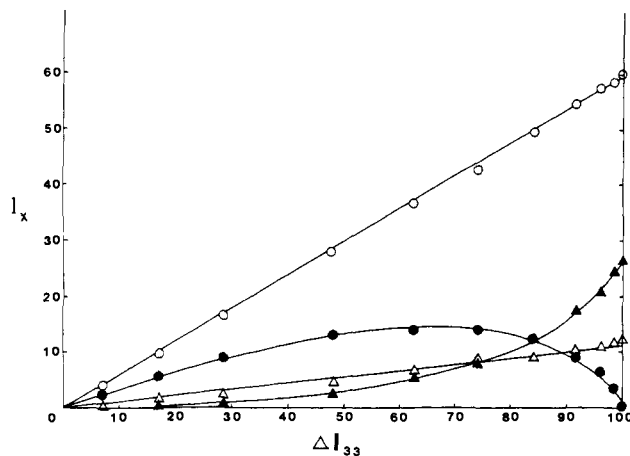
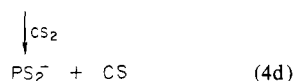
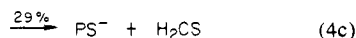
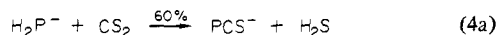


Figure 2. Relative intensity of product ions vs. percent conversion of H_2P^- for the reaction $\text{H}_2\text{P}^- + \text{CS}_2$: (O), PCS^- ; (Δ), H_2PCS_2^- ; (\bullet), PS^- ; (\blacktriangle), PS_2^- . Slope of the line for $\text{PCS}^- = 0.60$, for $\text{H}_2\text{PCS}_2^- = 0.11$, and for PS^- (extrapolated to zero conversion) = 0.29 (0.3 torr He, 298 K).

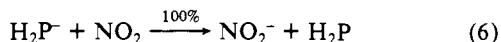
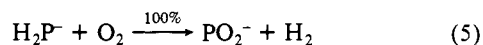
count, it appears that $\leq 5\%$ of the reaction yields HS^- . At this low level the m/z 34 sulfur isotope peak (4.22%) is not above the noise. The rate constant for the reaction with OCS , $k = 3.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is determined at low conversion where curvature of the kinetic plot does not interfere.

Phosphide reacts with carbon disulfide with a rate constant of $k = 1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to give the products shown in eq 4. The major product PCS^- is a phosphorus analogue of

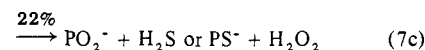
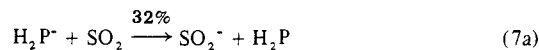


thiocyanate; again, formation of the conjugate acid–base pair, $\text{HS}^- + \text{HPCS}$, is possible, though no significant curvature was observed in these kinetic plots. The adduct H_2PCS_2^- represents 11% of the reaction product. The other products PS^- and PS_2^- (eq 4c,d) have no counterparts in the amide reactions. The anion of metaphosphorothious acid, PS^- , is formed as 29% of the product mixture; this species is apparently very reactive, generating PS_2^- , the anion of metaphosphorodithious acid, upon further reaction with CS_2 . This latter product was a bit perplexing at first, since there is no reasonable mechanism for forming it as a primary product (the neutral product would be methylene, H_2C). However, the branching ratio plot (Figure 2) clearly indicates that PS_2^- is a secondary product ion formed from the precursor PS^- .

The reaction of phosphide and oxygen gives only one ion product (eq 5) PO_2^- , the metaphosphite anion, with a rate constant of $k = 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Reaction with nitrogen dioxide also gives only one product (eq 6), NO_2^- , by electron transfer, which proceeds at about the gas kinetic rate, $k = 1.3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

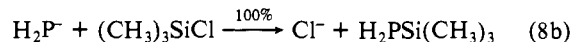
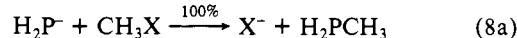


Part of the reaction of phosphide with sulfur dioxide also involves electron transfer to give SO_2^- (eq 7a), while chemical reaction gives PSO^- , PO_2^- (or PS^-), and H_2PSO_2^- . PSO^- is particularly interesting since it is the phosphorus analogue of NSO^- , an ion recently generated in this laboratory.⁶ Since both PO_2^- and PS^- have the same mass to charge ratio and since the signal to noise in this experiment was not sufficient to indicate the presence of the sulfur isotope, we cannot at this time distinguish between the two. Formation of a small amount ($\leq 3\%$) of m/z



33 is again implicated from curvature of the kinetic plots for loss of H_2P^- , and this could be either from $\text{PO}_2^- + \text{H}_2\text{S} \rightleftharpoons \text{HPO}_2 + \text{HS}^-$ or from $\text{PS}^- + \text{H}_2\text{O}_2 \rightleftharpoons \text{HPS} + \text{HO}_2^-$, possibly with subsequent reaction $\text{HO}_2^- + \text{PH}_3 \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{P}^-$, since HO_2^- is a stronger base than H_2P^- . The reaction rate constant is $2.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Reaction of phosphide with the methyl halides, CH_3X , and with trimethylsilyl chloride, $(\text{CH}_3)_3\text{SiCl}$, generates the halide ion as the only ion product (eq 8). The rate constant for reaction



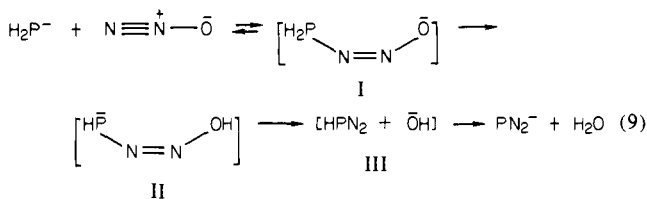
increases as one progresses down the family of halogens, from Cl to I. The rate constant is equal to the collision rate (k_{ADO}) with $(\text{CH}_3)_3\text{SiCl}$ (Table II).

Finally, no reactions were observed between phosphide and the following compounds: D_2O , ethylene oxide, dimethyl ether, carbon monoxide, and tetramethylsilane.

The rate constants for the reactions of H_2N^- and HO^- with PH_3 , to generate H_2P^- , were also measured. For both reactions, $k = 2.0 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Discussion

A. Reaction of H_2P^- with N_2O . The formation of PN_2^- from the reaction of H_2P^- and N_2O presumably arises through a mechanism similar to that proposed for the analogous formation of N_3^- from the reaction of H_2N^- and N_2O (eq 9).⁶ Attracted



by ion–dipole and ion–induced dipole forces, phosphide attacks the more electrophilic end of nitrous oxide forming the complex I. The excess internal energy in I, acquired through formation of the phosphorus–nitrogen bond, is not completely removed by collisions with helium since the adduct I is not detected. Instead, the complex either redissociates to H_2P^- and N_2O or is stabilized by further reaction. Intramolecular proton transfer from phosphorus to oxygen generates II followed by loss of HO^- to produce a new ion–dipole complex III, which, after proton abstraction by HO^- , dissociates to form PN_2^- and H_2O . We are not aware of any reports of the PN_2^- ion in the gas phase; this species has been synthesized in condensed phase in the forms of amorphous $(\text{HPN}_2)_n$ ⁸ and the salts LiPN_2 , NaPN_2 , and KPN_2 .^{9,10} It is not clear, however, whether these condensed phase examples have the NPN^- structure or, as we believe is the case in our gas-phase experiments, the PNN^- structure.

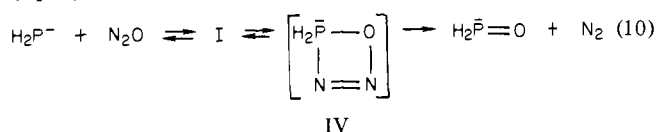
Most of the reaction (92%) between phosphide and nitrous oxide, however, proceeds to give the product H_2PO^- ; the analogous ion is not seen in the amide reaction. Direct attack of H_2P^- on the oxygen of N_2O with displacement of N_2 is a possibility, but formation of this product can also be rationalized by using the initial nucleophilic attack of H_2P^- on the nitrogen end of N_2O

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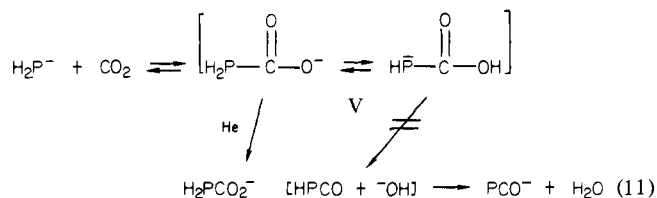
(eq 10). Formation of a four-membered cyclic intermediate IV,



reminiscent of the intermediate proposed for the Wittig reaction, is feasible due to the strength of the phosphorus-oxygen bond. Since the P-O bond ($\sim 97 \text{ kcal mol}^{-1}$)¹¹ is about twice as strong as the N-O bond ($\sim 48 \text{ kcal mol}^{-1}$),¹¹ the possibility of such an intermediate in the phosphide reaction, but not in the amide reaction, is reasonable. Expulsion of nitrogen gives $\text{H}_2\text{P}=\text{O}$, the anion of phosphine oxide.

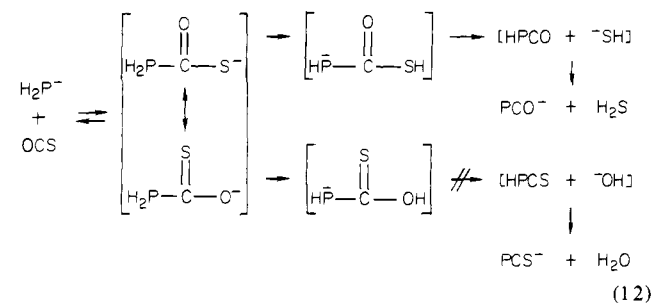
There are two factors that can account for the diminished reactivity of phosphide compared to that of amide with N_2O (amide is at least 100 times more efficient). First, phosphide is considerably less basic and less nucleophilic than amide ($\text{PA}(\text{H}_2\text{P}^-) = 370 \text{ kcal mol}^{-1}$; $\text{PA}(\text{H}_2\text{N}^-) = 404 \text{ kcal mol}^{-1}$).¹² This difference is evidenced in slower $\text{S}_{\text{N}}2$ reactions of phosphide with the methyl halides. Second, cleavage of II to form the ion-dipole pair III (eq 9) is expected to be much more difficult in the phosphide case since HO^- is a much stronger base than H_2P^- but a weaker base than H_2N^- . It appears that the lower nucleophilicity of H_2P^- is the major contributing factor since, even though the phosphide reaction has an additional pathway available to it (eq 10) that is not influenced by the relative basicities of H_2P^- and HO^- , the overall reaction nonetheless proceeds much less efficiently than with amide.

B. Reactions of H_2P^- with CO_2 , OCS , and CS_2 . Many of the same arguments presented to explain the reactions and reactivity of phosphide with nitrous oxide also suffice to rationalize those with carbon dioxide, carbonyl sulfide, and carbon disulfide. Thus initial nucleophilic attack of H_2P^- on the carbon of CO_2 produces the intermediate V (eq 11) that, though it does not react further,



can be stabilized by collisions with helium to yield the adduct H_2PCO_2^- . The difficult step in the reaction that would form PCO^- must be the loss of HO^- , a much stronger base than H_2P^- , since proton transfer from phosphorus to oxygen should be exothermic. By contrast the H_2N^- reaction yields 100% NCO^- by a similar, though thermodynamically more favorable, pathway.⁶

The reaction of phosphide with carbonyl sulfide lends further support to the suggestion that the loss of HO^- is the barrier to reaction. Either PCO^- or PCS^- could be formed in the reaction, but only PCO^- is observed (eq 12). Since proton transfer to



oxygen should be as easy as that to sulfur, PCS^- formation would also be expected if this were the important factor. However, cleavage to yield HS^- , a slightly weaker base than H_2P^- , is certainly

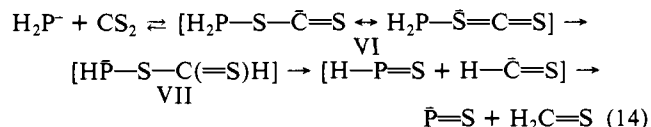
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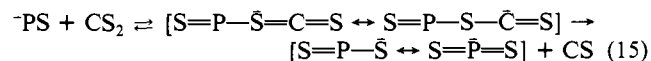
thermodynamically more favorable than cleavage to yield the stronger base HO^- , and therefore formation of the product $\text{PCO}^- + \text{H}_2\text{S}$ is the overall preferred pathway. Sulfur transfer to form H_2PS^- apparently arises from initial nucleophilic attack at the sulfur of OCS , with expulsion of CO (eq 13), again analogous $\text{H}_2\text{P}^- + \text{OCS} \rightleftharpoons [\text{H}_2\text{P}-\text{S}=\text{C}=\text{O} \leftrightarrow \text{H}_2\text{P}-\text{S}-\text{C}=\text{O}] \rightarrow \text{H}_2\text{PS}^- + \text{CO} \quad (13)$

to the reaction of amide. Finally, adduct formation, requiring stabilization by collisions with the buffer gas, is now a relatively minor process.

The first two reactions shown for phosphide and carbon disulfide (eq 4a,b) follow a course similar to that described for OCS . Reaction 4a comes about by addition, proton transfer, and loss of HS^- . Final proton transfer gives PCS^- and H_2S . Adduct formation (eq 4b) is again the minor process. Although the sulfur-transfer reaction, which would produce H_2PS^- and H_2NS^- from H_2P^- and H_2N^- , respectively, is not observed, the formation of the unique PS^- anion can be rationalized through a similar attack on sulfur (eq 14). The intermediate VI may not expel



CS for thermodynamic reasons, but proton transfer may compete to form VII, which after cleavage and final proton transfer gives PS^- and H_2CS . Such a reaction is not competitive in the OCS case since expulsion of CO is more favorable. The species PS^- must be quite reactive since it is the only product ion encountered in this study which reacts further with the neutral reagent. This secondary reaction involves sulfur transfer from CS_2 to give PS_2^- . A possible pathway for this process is shown in eq 15.



Though the reactions of H_2P^- with the series CO_2 , OCS , and CS_2 exhibit dramatically increasing rate constants (Table II), owing to increasingly facile product channels, nonetheless they are all considerably slower than the analogous reactions of the stronger base H_2N^- .

We believe that none of these ions has been observed in the gas phase previously. H_2PSH , the conjugate acid of H_2PS^- , was trapped at -196°C as a product of the glow discharge reaction between PH_3 and H_2S but decomposed upon warming to -130°C .¹³ $\text{HO}-\text{C}\equiv\text{P}$, phosphinidyne methanol, a candidate for the conjugate acid of PCO^- , has been prepared.¹⁴⁻¹⁶ There are also a few examples of metal salts of PS^- and PS_2^- , namely, HgPS_2 , AgPS_2 ,¹⁷ TIPS ,¹⁸ and $\text{In}(\text{PS}_2)_2$,¹⁹ prepared by thermal reactions of the elemental metals, phosphorus and sulfur, at elevated temperatures ($900\text{--}1200^\circ\text{C}$). We have found no examples of, nor references to, PCS^- or its conjugate acid or any of the adducts H_2PCO_2^- , H_2PCOS^- , and H_2PCS_2^- .

C. Reactions of H_2P^- with O_2 , NO_2 , and SO_2 . These reactions differ somewhat from those previously discussed in that they partly or exclusively involve electron transfers or oxidations. The reaction of phosphide with oxygen results in complete oxidation of phosphorus, forming the metaphosphite anion PO_2^- and expelling a molecule of hydrogen. Although many spectroscopic studies have been conducted on salt-matrix-isolated PO_2^- ,²⁰ there are no

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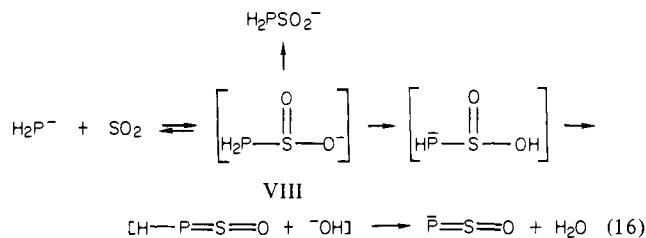
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gas-phase examples except for studies of the thermodynamic properties of gaseous EuPO_2^{21} and of gaseous NaPO_2^{22} . Nitrogen dioxide, with its very large electron affinity of 2.4 eV,²³ readily accepts an electron from H_2P^- at about the collision rate, giving solely NO_2^- and H_2P ($\text{EA}(\text{H}_2\text{P}) = 1.25 \text{ eV}$).^{24,25}

Approximately one third of the reaction between phosphide and sulfur dioxide also proceeds by electron transfer. However the remainder of the reaction occurs by pathways similar to those described for OCS and CS_2 . The PSO^- ion is formed by initial nucleophilic attack at sulfur, proton transfer from phosphorus to oxygen, loss of HO^- , and finally proton abstraction (eq 16); al-



ternatively, collisional stabilization of the intermediate VIII gives the adduct H_2PSO_2^- . The PSO^- ion has been observed in the negative ion mass spectra of the organophosphorus pesticides Dursban and Azinphos Methyl,²⁶ but we have found no examples of the adduct H_2PSO_2^- .

We cannot speculate confidently at this time as to whether the ion at m/z 63 is PO_2^- or PS^- (eq 7c), though we favor the former since loss of HS^- from some reactive complex should be more favorable, on a gas-phase acidity basis, than loss of HO_2^- . Either of the possibilities can, however, be tested. The two candidates for this product ion have been generated independently in other reactions, PS^- from phosphide and carbon disulfide and PO_2^- from phosphide and oxygen. Therefore a study of their subsequent ion-molecule reactions, for example, $\text{PS}^- + \text{CS}_2 \rightarrow \text{PS}_2^- + \text{CS}$,

may allow qualitative identification of the unknown species in the reaction of H_2P^- and SO_2 . We will report on developments in this area in forthcoming publications.

D. Reactions of H_2P^- with CH_3X and $(\text{CH}_3)_3\text{SiCl}$. Phosphide reacts with trimethylsilyl chloride at the collision rate presumably because of the ease with which silicon can accommodate a pentacoordinate intermediate. However, the reaction efficiency diminishes rapidly through the series $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl}$ (Table II). Since amide reacts rapidly with all the methyl halides and with trimethylsilyl chloride,²⁷ it is clear that phosphide is considerably less nucleophilic than amide. This supports the observation that phosphide reacts much less efficiently than amide with the molecules listed in Table II, whenever a nucleophilic mechanism is involved.

Conclusion

With this study we have accomplished several objectives. We have shown that phosphide reacts readily with a variety of molecules via familiar reaction mechanisms, including proton transfer, electron transfer, nucleophilic addition, and nucleophilic substitution. Many similarities exist between the reactions of phosphide and those of amide. However, we have elucidated some distinct differences in both the reactivity and mechanism and have attributed these differences to properties such as basicity, nucleophilicity, bond strengths, and electron affinities. The reactions allow the gas-phase synthesis of many previously unknown phosphorus-containing anions. We plan to explore further the ion-molecule chemistry of these species including their reactivity, basicity, and nucleophilicity.

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Registry No. H_2P^- , 13937-34-3; N_2O , 10024-97-2; CO_2 , 124-38-9; OCS, 463-58-1; CS_2 , 75-15-0; O_2 , 7782-44-7; NO_2 , 10102-44-0; SO_2 , 7446-09-5; $(\text{CH}_3)_3\text{SiCl}$, 75-77-4; CH_3Cl , 74-87-3; CH_3Br , 74-83-9; CH_3I , 74-88-4.

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Association of Methyl Viologen and Its Cation Radical with Dihexadecyl Phosphate Vesicles

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Abstract: A strong association of methyl viologen with negatively charged DHP vesicles is demonstrated. This adsorption is probed with ESR spectroscopy which monitors the formation of the methyl viologen cation radical produced by UV irradiation. This interaction is shown to be electrostatic in nature since no association was observed with the positively charged dioctadecyldimethylammonium bromide vesicles. The interaction is of sufficient strength with DHP that the methyl viologen is not removed when the dispersion undergoes gel filtration on a Sephadex column. These results have important implications to vesicular studies which utilize methyl viologen as an electron acceptor.

Methyl viologen, MV^{2+} , is an electron acceptor frequently used in both homogeneous¹ and heterogeneous² solar-energy-converting

systems. The radical cation of methyl viologen, $\text{MV}^{\cdot+}$, usually formed via a photosensitized electron-transfer process can generate