from a study of the PES spectra of $ZP(OR)_3$ compounds (Z = lone pair or chalconide) in which it was concluded[22] that the first ionization potential in the spectrum of $P(OMe)_3$ is due to the phosphorus lone pair and not to the oxygen lone pairs as originally believed by these authors.[23] A PES study of **3** and its chalconide derivatives leads to the same conclusion.[24] Shifts in lone pair orbital energies of phosphites upon complexation to metal centers provides additional support for the new assignment.[25]

The relationship between the proton affinity and ionization potential revealed in the present study indicates that the proton-affinity order is determined by differences in the abilities of the phosphites to assume a positive charge. This conclusion supports previous rationalizations of the basicity order, in which the trend is ascribed to differences in the interaction of the oxygen lone pairs with phosphorus.[2,4,26] The repulsive interaction of the phosphorus and oxygen lone pairs destabilizes the phosphorus lone pair in the neutral phosphite,[2,27] while π bonding between oxygen and phosphorus in the protonated phosphite and the molecular ion delocalizes the positive charge.[2,24,28] Both of these interactions serve to decrease the ionization potential and increase the proton affinity. The changes in geometry which accompany increasing constraint of the phosphite alter the spatial orientation and hybridization of the oxygen lone pair orbitals such that their interactions with the phosphorus lone pair and π-bonding orbitals are weakened.[2] The decrease in the basicity of an equatorial vs. an axial phosphorus lone pair in **8** and **9** may also be ascribed to a weakening of these interactions.[2,24,27] The extent to which phosphorus d orbitals are important in the π-bonding effects may well be small, however.

The 5 kcal/mol increase in proton affinity upon methyl substitution in **1** is large in comparison with the effect of methyl substitution remote from the site of protonation in other compounds. For example, substitution of CH_3 for H in RCH_2CHO and RCH_2CN raises the proton affinity by about 3 kcal/mol.[11] Although not accurately determined, the increase of 2.7 kcal/mol resulting from methyl substitution in **3** appears "normal" if not slightly on the high side. The existence of three pathways for through-bond interactions between the methyl group and the phosphorus atom in the bicyclic molecule may augment the methyl effect relative to that in acyclic compounds.

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Nucleophilic Reactions of Anions with Trimethyl Phosphate in the Gas Phase by Ion Cyclotron Resonance Spectroscopy

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Abstract: The gas-phase ion-molecule reactions of several negative ions (SF_6^-, SF_5^-, SO_2F^-, F_2^-, F^-, CF_3Cl^-, Cl^-, CD_3O^-, DNO^-, OH^-, and NH_2^-) with trimethyl phosphate are investigated using ion cyclotron resonance techniques. Nucleophilic attack on $OP(OCH_3)_3$ occurs chiefly at carbon, resulting in displacement of $O_2P(OCH_3)_2^-$. This behavior contrasts with that observed in solution, where attack at phosphorus is favored for hard nucleophiles. This difference is ascribed to solvation energetics for the intermediates involved in the two reactions. The failure of SF_6^- to transfer F^- to $OP(OCH_3)_3$ places an upper limit of 11 ± 8 kcal/mol on the fluoride affinity of $OP(OCH_3)_3$). The significance of the results for the negative chemical ionization mass spectrometry of phosphorus esters is briefly discussed.

Bimolecular nucleophilic substitution reactions occupy an important place in the chemistry of phosphorus compounds.[1] All classes of phosphorus compounds are susceptible to nucleophilic attack. The esters of phosphoric acid are of special interest because of their biological significance. Some are essential to life processes, while the toxicology of others has

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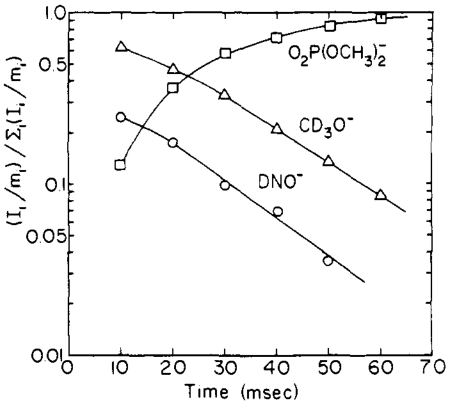


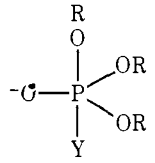
Figure 1. The temporal variation of ion abundances in a mixture of $OP(OCH_3)_3$ (partial pressure 9.0×10^{-7} Torr) and CD_3ONO following a 10-ms, 70-eV electron pulse.

commanded attention.[2] The site of nucleophilic attack may be the phosphorus atom or the α carbon of the ester group.[3,4] Attack at phosphorus results in transesterification (reaction 1), while attack at carbon displaces the phosphate diester anion (reaction 2).

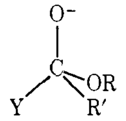
$$Y^- + OP(OR)_3 \rightarrow OP(Y)(OR)_2 + OR^- \quad (1)$$

$$Y^- + OP(OR)_3 \rightarrow O_2P(OR)_2^- + RY \quad (2)$$

The site of attack follows predictions of the theory of hard and soft reagents.[3,5,6] Hard nucleophiles (e.g., OH^-, F^-) attack at phosphorus, while soft nucleophiles (e.g., Cl^-, H_2O) attack at carbon. Reaction 1 is first order in nucleophile and substrate and occurs with inversion of configuration.[4,7] The pentacoordinate species I is proposed to exist during the course of the reaction.[8] This species is analogous to the tetrahedral intermediate II, formed by nucleophilic attack on carboxylic esters.



I



II

Earlier opinion[10] that species such as I are unstable transition states has given way to the view that in many cases they are intermediates.[8,11-13] Reaction 2 is considered to be an S_N2 displacement at carbon.[4,14]

Ions similar to species II have been generated at low pressure in an ion cyclotron resonance (ICR) spectrometer by halide transfer from a donor anion to a carbonyl compound e.g.[15]

$$Cl_2^- + CH_3COCl \rightarrow CH_3COCl_2^- + Cl \quad (3)$$

A halide adduct with a phosphorus compound has recently been prepared. SF_6^- and SF_5^- transfer F^- to OPF_3 to give the pentacoordinate anion OPF_4^-.[16] The binding energy of F^- to OPF_3 was determined by ICR techniques to be 59 ± 1 kcal/mol.[16] Studies of the gas-phase hydrolysis of phosphorus esters have been briefly described and compared to related solution studies.[17]

This paper reports ICR investigations of the reactions of a number of anions with trimethyl phosphate. Mechanisms are proposed and compared with those of other gas-phase nucleophilic reactions. Differences between the solution and gas-phase reactivities of trimethyl phosphate are discussed in terms of solvation effects. The implications of these results for negative chemical ionization mass spectrometry of phosphorus esters are discussed.

Experimental Section

Experiments were performed using an ICR spectrometer built in this laboratory. The general features of ICR instrumentation and experimental techniques have been described previously.[18,19] All reaction pathways were verified in double-resonance experiments.[18]

Pressure measurements were made using a Schulz-Phelps gauge located adjacent to the ICR cell. This gauge is calibrated for each gas for a given emission current (5 μA) and magnetic field (6 kG) against an MKS Instruments Baratron Model 90H1-E capacitance manometer in the region 10^{-5}–10^{-3} Torr where linear variation of gauge current with pressure is observed. Pressures in the trapped ion experiments were in the range 10^{-7}–10^{-6} Torr. Experiments in the drift mode were carried out at pressures of $\sim 10^{-5}$ Torr. The uncertainty in the rate constants, estimated to be ±20%, is due principally to uncertainties in pressure measurement.

Ion concentrations were approximately 10^5 ions cm^{-3}. Neutral products from ion-molecule reactions are thus less than one part in 10^5 and do not participate further in observed reactions.

Negative ions were generated by electron capture or dissociative electron capture from the following neutral species: SF_6 (SF_6^-, SF_5^-, 70 eV), SO_2F_2 (SO_2F^-, F_2^-, and F^-, 3 eV), NF_3 (F^-, 70 eV), CCl_4 (Cl^-, 70 eV), CF_3COCl (Cl^-, and CF_3Cl^-, 70 eV), CD_3ONO (CD_3O^- and DNO^-, 70 eV), H_2O (OH^-, 5 eV), and NH_3 (NH_2^-, 4 eV). The major ions produced from each species and the electron energies employed are given in parentheses.

Methyl nitrite was prepared by literature methods.[20] All other chemicals were commerical, reagent grade materials and were used as supplied.

Results

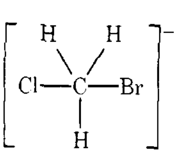
Electron impact of trimethyl phosphate alone at electron energies varying from 0 to 70 eV produced no abundant negative ions at the pressures employed in these experiments (10^{-6}–10^{-5} Torr).

The ions SF_6^-, SF_5^-, SO_2F^-, and F_2^- gave no reaction with $OP(OCH_3)_3$. In particular, no halide transfer or direct attachment processes to give ion I were observed. Failure to observe F^- transfer from SF_5^-, SO_2F^-, F_2^-, and SF_6^- to $OP(OCH_3)_3$ permits the assignment of upper limits on the fluoride affinity of $OP(OCH_3)_3$ of 54 ± 12, 45, 29 ± 3, and 11 ± 8 kcal/mol, respectively.[16]

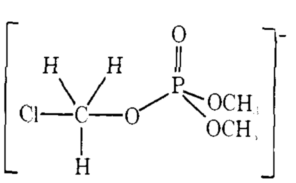
The ion CF_3Cl^- transfers Cl^- to $OP(OCH_3)_3$:

$$CF_3Cl^- + OP(OCH_3)_3 \rightarrow OP(OCH_3)_3Cl^- + CF_3 \quad (4)$$

Therefore, the chloride affinity of $OP(OCH_3)_3$ is greater than that of CF_3. The chloride affinity of CF_3 is very low. Even methyl bromide will accept a chloride ion from CF_3Cl^- to form ion III.[21] It is possible that the adduct of Cl^- with $OP(OCH_3)_3$



III



IV

does not assume structure I, but rather structure IV or possibly a species where the bonding is even less specific than in I or IV.

The ions F^-, CD_3O^-, and DNO^- displace the phosphate diester anion from trimethyl phosphate:[22]

$$F^- + OP(OCH_3)_3 \rightarrow O_2P(OCH_3)_2^- + CH_3F \quad (5)$$

$$CD_3O^- + OP(OCH_3)_3 \rightarrow O_2P(OCH_3)_2 + CH_3OCD_3 \quad (6)$$

$$DNO^- + OP(OCH_3)_3 \rightarrow O_2P(OCH_3)_2^- + CH_3D + NO \quad (7)$$

Figures 1 and 2 illustrate the variation of the abundances of these ions with time. The rate constants determined for these reactions are $k_5 = 1.6 \times 10^{-9}$, $k_6 = 1.4 \times 10^{-9}$, and $k_7 = 1.6$

$\times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. No deuterium incorporation into the phosphate diester anion formed in reaction 6 occurs. The site of attack in this reaction must, therefore, be the carbon atom. If attack at phosphorus were to occur, giving the intermediate I, pseudorotation[23] in the chemically activated intermediate would very likely scramble the methoxy groups in a time much shorter than the lifetime of the intermediate toward loss of dimethyl ether, such that deuterium incorporation into the ionic product would be observed.

Cl^- produced in a mixture of CCl_4 and $OP(OCH_3)_3$ was nonreactive. However, when the signal intensity of $O_2P(OCH_3)_2^-$ in a mixture of $OP(OCH_3)_3$ and CD_3ONO was monitored, a positive double-resonance signal from Cl^-, which was present as a contaminant, was observed. This suggests that the displacement of $O_2P(OCH_3)_2^-$ from $OP(OCH_3)_3$ by Cl^- (reaction 8) is slightly endothermic, but can occur with translationally excited Cl^-.

$$Cl^- + OP(OCH_3)_3 \rightarrow O_2P(OCH_3)_2^- + CH_3Cl \quad (8)$$

The phosphate diester anion is the major product ion observed in drift mode mass spectra of mixtures of $OP(OCH_3)_3$ with H_2O and with NH_3. Double-resonance experiments established that this ion is formed by reaction of OH^- and NH_2^- (reactions 9 and 11). OH^- and NH_2^- also displace CH_3O^- from $OP(OCH_3)_3$ (reactions 10 and 13). The amount of CH_3O^- formed in these reactions is uncertain, because CH_3O^- subsequently reacts rapidly to form $O_2P(OCH_3)_2^-$ (reaction 6). The percentages given for CH_3O^- represent lower limits. However, reaction times in the drift mode are short (a few milliseconds) and the product distribution should, therefore, depend principally on the rate constants of the primary reactions. Double-resonance experiments failed to produce any evidence for reaction 6 under these low conversion conditions. The product ion $OP(OCH_3)_2^-$ also results from reaction of NH_2^- (reaction 12). This reaction probably occurs by proton transfer from $OP(OCH_3)_3$ followed by loss of CH_2O from $OP(OCH_3)_2(OCH_2)^-$. The observation of reaction 12 and the failure of OH^- to undergo a similar reaction suggests that the proton affinity of $OP(OCH_3)_2(OCH_2)^-$ lies between PA(OH^-) = 390.7 kcal/mol[24,25] and PA(NH_2^-) = 403.8 kcal/mol.[24,25]

$$OH^- + OP(OCH_3)_3 \xrightarrow{85\%} O_2P(OCH_3)_2^- + CH_3OH \quad (9)$$

$$\xrightarrow{15\%} CH_3O^- + OP(OH)(OCH_3)_2 \quad (10)$$

$$NH_2^- + OP(OCH_3)_3 \xrightarrow{75\%} O_2P(OCH_3)_2^- + CH_3NH_2 \quad (11)$$

$$\xrightarrow{20\%} OP(OCH_3)_2^- + NH_3 + CH_2O \quad (12)$$

$$\xrightarrow{5\%} CH_3O^- + OP(NH_2)(OCH_3)_2 \quad (13)$$

Discussion

Reaction Mechanism. As in solution the reactions of anions with trimethyl phosphate in the gas phase can be accommodated by a mechanism in which the nucleophile attacks at phosphorus or at carbon (Scheme I). Although the stability of the intermediates proposed in Scheme I are not known, their energy must be less than the heats of formation of the reactants. It is not required that the proposed intermediates be minima in the potential energy surface, however.[26] Attack at phosphorus yields a pentacoordinate intermediate V, which can decompose to the reactants or expel CH_3O^-, if displacement of CH_3O^- by Y^- is exothermic. Displacement of CH_3O^- is observed for two of the anions in this study, OH^- and NH_2^-, but not for Cl^- and F^-. This suggests that the heterolytic bond dissociation energy, $D(OP(OCH_3)_2^+\text{-}Y^-)$ increases in the order Cl^-, $F^- < CH_3O^- < OH^-$, NH_2^-. This order parallels the proton-affinity order $Cl^- < F^- < CH_3O^- < OH^- < NH_2^-$.[24-28]

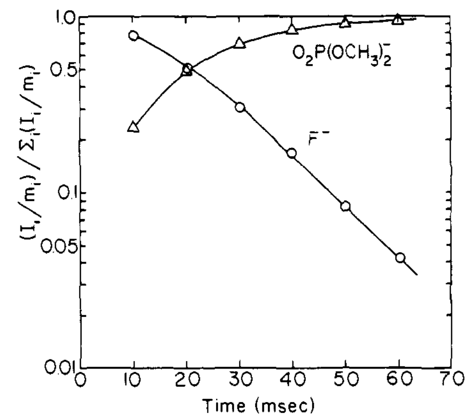
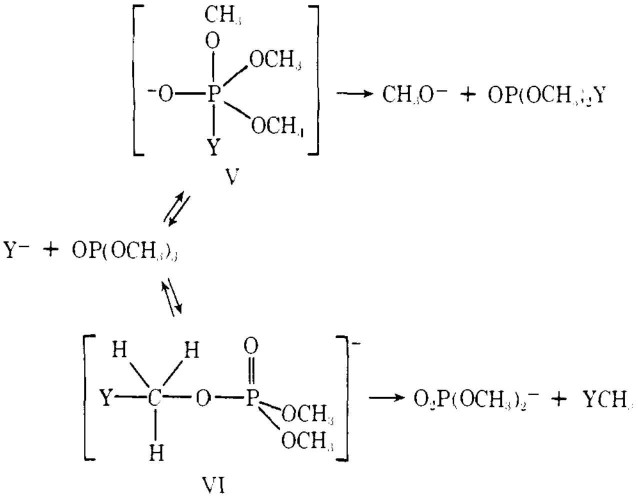


Figure 2. The temporal variation of ion abundances in a mixture of $OP(OCH_3)_3$ (partial pressure 1.35×10^{-6} Torr) and NF_3 following a 10-ms, 70-eV electron pulse.

Scheme I



Attack at carbon leads to displacement of $O_2P(OCH_3)_2^-$ via VI. Perhaps the most noteworthy result in this study is the fact that even OH^- and NH_2^-, which are able to displace CH_3O^-, react principally at carbon. This stands in contrast to the behavior of phosphate esters in solution, where hard nucleophiles react at phosphorus.[3,5] Differences in the relative importance of the two reaction pathways in the gas phase and in solution may be due to differences in the solvation energies of the reaction intermediates. The intermediate arising from attack at phosphorus (species I) has a relatively localized charge on the phosphoryl oxygen and may benefit from solvation more than the S_N2 transition state, which has a more delocalized charge distribution. This reasoning suggests that the energetics of attack at phosphorus will be improved by solvation relative to that of attack at carbon.

Analogous differences in the reactivities of anions with carboxylic esters in solution and in the gas phase have been noted.[29] In gas-phase processes similar to reaction 9, OH^- reacts with several carboxylic esters to give the carboxylate anion:[29]

$$OH^- + RCOOR' \rightarrow RCOO^- + R'OH \quad (14)$$

Although there are known cases of nucleophilic attack on the alkyl group, the more usual product in solution hydrolysis reactions of carboxylic esters is the alkoxide anion:

$$OH^- + RCOOR' \rightarrow RCOOH + R'O^- \quad (15)$$

Alkoxide anions are formed in gas-phase reactions of OH^- with *tert*-pentyl acetate and methyl octanoate, but are not present with methyl, ethyl, and *n*-propyl acetate.[29] Riveros and co-workers have reported reactions of F^- and OH^- with alkyl formates which yield the formate anion:[30]

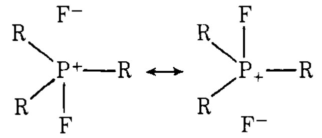
$$F^- + HCOOR \rightarrow HCOO^- + RF \qquad (16)$$

$$OH^- + HCOOR \rightarrow HCOO^- + ROH \qquad (17)$$

The relative solvation energies of the intermediates (species II and an S_N2 transition state) may be used to rationalize the solution and gas-phase reactivities of carboxylic esters as for the phosphorus esters.

$PA(O_2P(OCH_3)_2^-)$. The observation of reaction 5 permits an upper limit of −246 kcal/mol to be placed on the heat of formation of $O_2P(OCH_3)_2^-$. If reaction 8 is endothermic, a lower limit of −275 kcal/mol may be set for this heat of formation.[31] Combining a heat of formation of $O_2P(OCH_3)_2^-$ of -260 ± 15 kcal/mol with an estimated heat of formation for $HOPO(OCH_3)_2$ of -243 ± 15 kcal/mol[32] yields a proton affinity of $O_2P(OCH_3)_2^-$ of 350 ± 30 kcal/mol. This is in the same range as the proton affinities of other reasonance-stabilized anions (e.g., $PA(CH_3CO_2^-) = 345.8$ kcal/mol).[33]

Fluoride Affinity. The large difference in the fluoride affinities of $OP(OCH_3)_3$ [$D(OP(OCH_3)_3\text{-}F^-) < 11 \pm 8$ kcal/mol] and OPF_3 [$D(OPF_3\text{-}F^-) = 59 \pm 1$ kcal/mol] is an illustration of the ability of highly electronegative substituents to promote valence expansion of second-row elements. The fluoride affinities of the fluoromethylsilanes, which increase in the order $(CH_3)_3SiF \ll (CH_3)_2SiF_2 < CH_3SiF_3 < SiF_4$, provide another example.[34] Most stable neutral penta- and hexacoordinate compounds of phosphorus and sulfur are also substituted with highly electronegative substituents (e.g., PF_5, SF_6, SOF_4). The ability of elements below the first row to form more bonds than are permitted by the octet rule has been attributed to the involvement of d orbitals in bond formation[35,36] or to the formation of a three-center, four-electron bond.[37-39] The stabilization of hypervalent compounds by highly electronegative substituents is accounted for by both of these bonding descriptions. It has been proposed[35,36] that electronegative substituents contract the otherwise diffuse d orbital more than s and p valence orbitals and thus improve their overlap with other bonding orbitals. Electronegative substituents are also expected to stabilize the resonance structures of a three-center, four-electron bond.[39]



Negative Chemical Ionization Mass Spectrometry. The development of analytical techniques for phosphorus esters is important, because of the biological significance of these molecules. The results presented here are relevant to the design of negative chemical ionization mass spectrometric[29,40,41] schemes for the detection of phosphorus esters. It is desirable to produce peaks in a mass spectrum which indicate the molecular weight of the sample and which provide structural information. Chloride ion attachment has been used to produce the quasi-molecular ion $[M + Cl]^-$ with a variety of substrates.[41-43] The adduct of Cl^- and trimethyl phosphate was observed in this study (reaction 4). No bimolecular pathway for formation of the F^- adduct was discovered, but formation of this adduct by direct attachment at higher pressure may be possible. However, the formation of halide-phosphorus ester adducts under chemical ionization conditions requires a reagent gas with a halide affinity less than that of the phosphorus ester.

The most prominent process observed with trimethyl phosphate, displacement at carbon, could be used to obtain ions which provide structural information. Reaction of an appropriate reagent ion (e.g., OH^- or CH_3O^-)[29,40] with a phosphorus compound with different ester groups, $OP(OR)(OR')(OR'')$, is expected to give phosphate diester anions, whose masses are characteristic of the molecular weights of the ester groups.

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