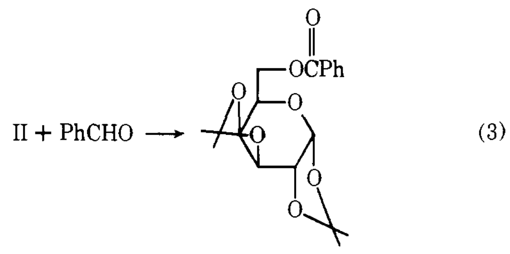
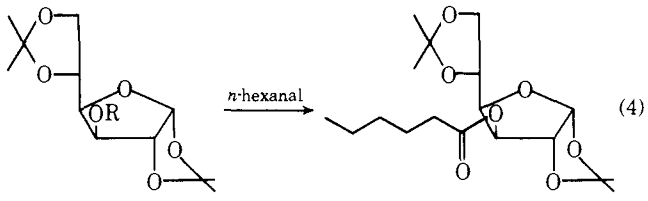
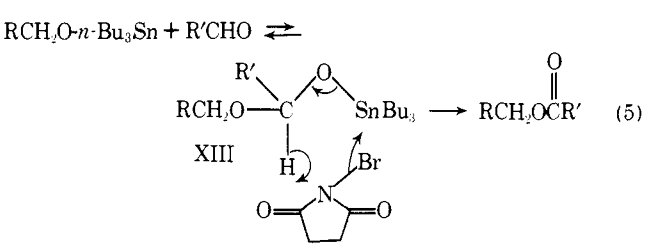


IX



X, R = H
XI, R = n-Bu$_3$Sn

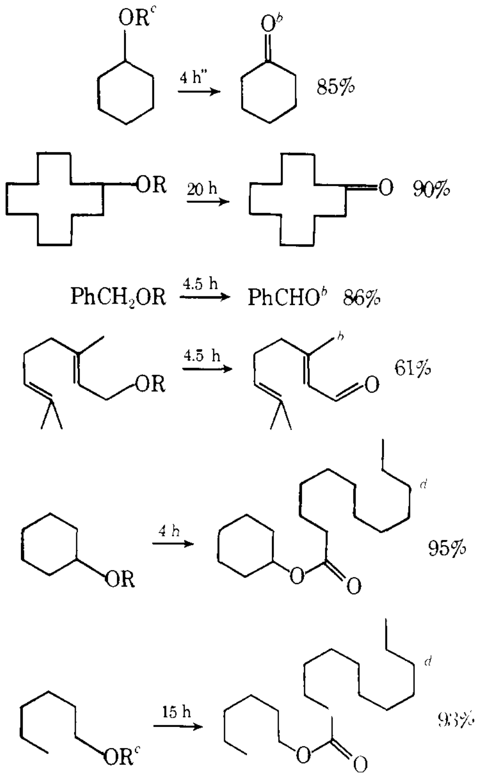
XII



pounds other than carbohydrates was examined by using aliphatic alcohols. Preliminary results are shown in Scheme I.

The results described above indicate the following aspects of this reaction: (1) in the absence of added aldehyde, (i) primary alcohols (RCH$_2$OH) gave dimeric esters (RCH$_2$OCOR), (ii) primary alcohols of the benzylic or allyic type give aldehydes (RCHO), and (iii) secondary alcohols (R′R″CHOH) give ketones (R′R″CO); and (2) in the presence of added aldehyde (RCHO), (i) primary alcohols (R′CH$_2$OH), excluding benzyl or allyl, give esters (R′CH$_2$OCOR), and (ii) secondary alcohols (R′R″CHOH) give esters (R′R″CHOCOR).

Scheme I



[a] All reactions were performed at room temperature with 1 equiv of NBS in dry CCl$_4$. [b] Isolated and identified as 2,4-DNP. [c] R should be regarded as (n-Bu)$_3$Sn. [d] The reactions were performed in the presence of added n-dodecanal.

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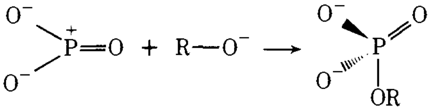
The Reactivity of Monomeric Metaphosphate

Sir:

The postulated intermediacy of the monomeric metaphosphate anion in the hydrolysis of phosphoric acid monoesters[1] and anhydrides[2] and in many biological phosphoryl transfer reactions[3] has evoked a steadily high level of interest in the chemistry of this species. There have been several recent successful demonstrations of a finite liefetime for PO$_3^-$ via chemical trapping experiments,[4] but the isolation of a compound with a stable phosphorus-oxygen (2p-3p) π-bond has not as yet been achieved. This reactivity is manifested as severe electron deficiency at phosphorus:



The instability associated with (2p-3p) π bonding is a general phenomenon[5] but its theoretical source is unclear.[6] It is the purpose of this communication to demonstrate the important contribution of the σ-system to the reactivity of monomeric metaphosphate and to initiate speculation as to the generality of our conclusions for all (2p-3p) π-bonded systems.

Ab initio SCF molecular orbital calculations[7] were performed for PO$_3^-$ and its congener NO$_3^-$. Bond length optimization led to a value of 1.543 Å for PO$_3^-$ and a total en-

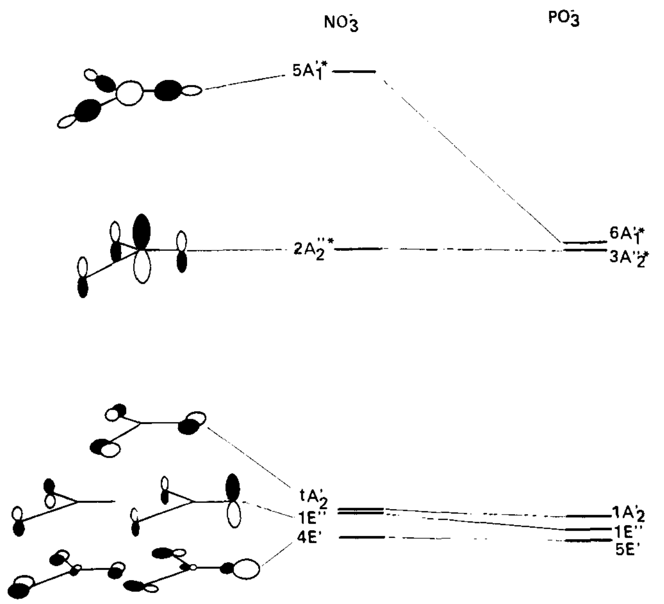


Figure 1. Frontier orbitals of PO_3^- and NO_3^-.

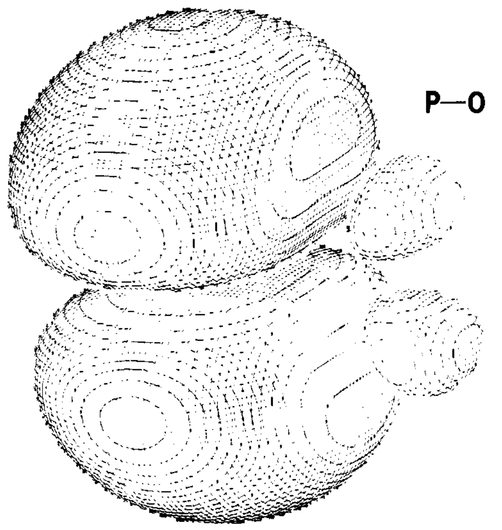


Figure 2. The π* ($3A_2''$) acceptor orbital of PO_3^-. Only one of the P-O bonds is included.

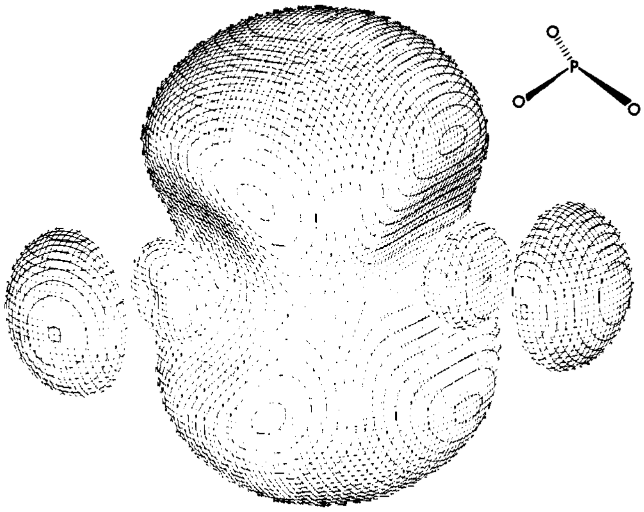


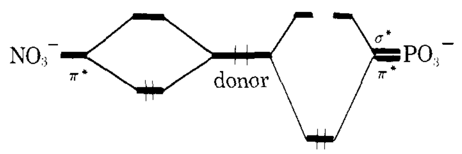
Figure 3. The σ* ($6A_1'$) acceptor orbital of PO_3^-. The cloud around one oxygen is hidden behind the phosphorus electron cloud.

ergy of −561.3076 hartree with a basis of Gaussian orbitals.[8] A bond length of 1.22 Å was assigned to NO_3^- [9] leading to a total energy of −277.2708 hartree.[8]

Comparison of the Mulliken overlap populations[10] in PO_3^- with those in NO_3^- provides an assessment of the viability of (2p-3p) π-bonding. The startling result is that the σ as well as the π contributions to the overlap population are larger in PO_3^-. The total overlap populations are 1.362 and 0.826 electrons per bond, whereas the π-contributions are 0.354 and 0.181 for PO_3^- and NO_3^-, respectively. The large P-O populations in metaphosphate reflect participation of d orbitals[11] consistent with a recent calculation on orthophosphoric acid.[12] While bond strengths need not completely parallel overlap populations, this dramatic difference between PO_3^- and NO_3^- compels a search for a kinetic rather than a thermodynamic source of the former's instability.

Klopman's perturbation theory of donor-acceptor interactions[13] is an ideal framework within which to attack this problem. The Mulliken analysis reveals a charge of +1.35 at the phosphorus. The simple conclusion that the reactivity is "charge controlled"[13] is invalid, however, because (a) the long range interactions will be dominated by the negative charge on the ion as a whole and (b) the less electrophilic phosphorus in orthophosphoric acid bears a larger positive charge (+1.76) (with a similar basis set).[12] An "orbital controlled"[13] reactivity presents itself as an attractive alternative.

The seat of electrophilicity in an "orbital controlled" ("soft") Lewis acid is in its low energy unoccupied molecular orbitals. The lower the energy of such an MO the more advantageous for it to accept the electrons of an approaching Lewis base. The three highest occupied and two lowest unoccupied levels of NO_3^- and PO_3^- are depicted in Figure 1. The isolation of the π* level ($2A_2''$) in NO_3^- is quite general for π-bonded species consisting of only second period elements. As a consequence, approach of a nucleophile is exclusively perpendicular to the plane of a π-system,[13,14] an in-plane approach placing donor electron density in the nodal plane of the acceptor orbital. This situation is dramatically altered for PO_3^- due to the near degeneracy (0.022 hartree vs. 0.39 in NO_3^-) of the π* ($3A_2''$) level with a σ* ($6A_1'$) level (Figure 1). This allows efficient mixing of these two MO's under the influence of a symmetry breaking donor orbital perturbation, which, since the σ* orbital has density in the molecular plane, will accommodate a variety of reaction paths. Further, the donor-acceptor coupling involves a 3-orbital-2-electron interaction (analogous to the π-system of cyclopropenium cation) which is especially stabilizing:



A necessary condition for this enhanced reactivity in addition to the favorable energies of these acceptor orbitals is that they have their major contributions from basis functions centered at phosphorus and that this density be moderately diffuse; this assures a large cross-section for the reaction. Figures 2 and 3 are plots[15] of the 0.01 density surface for the acceptor orbitals of PO_3^-. They provide a representation of the size and shape of the hole into which the donor electrons fall. Clearly both the π* and σ* MO's will contribute to a large electrophilic reactivity at phosphorus.

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George Gibson, Mark Olson, and William Macarthur offered invaluable computational assistance. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. A generous grant of computer time by the SUNY at Binghamton Computer Center is also gratefully acknowledged.

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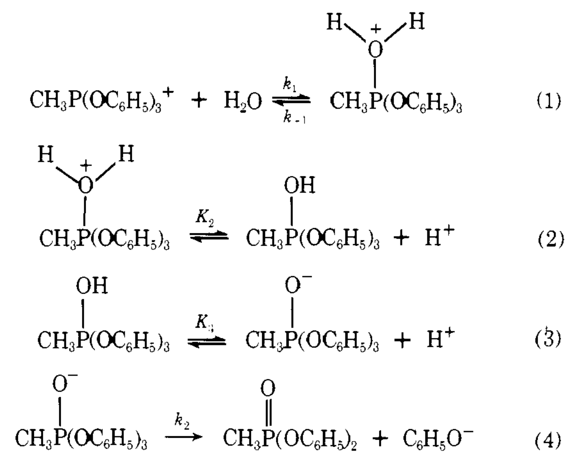
Kinetics and Mechanism of Hydrolysis of Aryloxyphosphonium Salts

Sir:

The hydrolysis of aryloxyphosphonium salts[1] such as $CH_3P(OC_6H_5)_3{}^+CF_3SO_3{}^-$ (A) may serve to model that of protonated aryl esters of phosphonic acids. The mechanism shown in Scheme I for the hydrolysis of methyltriphenoxyphosphonium triflate is supported by the kinetic data here reported.

The kinetics of hydrolysis can be followed spectrophotometrically in aqueous acetonitrile[1] by methods parallel to those previously published.[2] The rate of hydrolysis of $CH_3P(OC_6H_5)_3{}^+$ is too large to measure in pure water; the limit of our stopped-flow apparatus was reached with 8% water in acetonitrile.[3] The rate of the hydrolysis of the sterically hindered salt (B) methyltri(2,6-dimethylphenoxy)phosphonium triflate can, however,[4] be measured in aqueous acetonitrile solution to more than 50% water, and then extrapolated to pure water. Since the two salts show parallel behavior in acetonitrile solutions with low water content, the data (shown in Figure 1 and 2) allow a reasonable extrapolation of the rate of hydrolysis of A to pure water; note that the resulting rate constant of 0.6×10^4 s^{-1} exceeds by a power of ten any that can be measured for irreversible reactions in solution. We have as yet no explanation for the 10^6-fold increase in rate between 0.11 M and pure water.

Scheme I



$$CH_3P(OC_6H_5)_3{}^+ + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3\overset{\overset{H\diagdown\overset{+}{O}\diagup H}{|}}{P}(OC_6H_5)_3 \qquad (1)$$

$$CH_3\overset{\overset{H\diagdown\overset{+}{O}\diagup H}{|}}{P}(OC_6H_5)_3 \overset{K_2}{\rightleftharpoons} CH_3\overset{\overset{OH}{|}}{P}(OC_6H_5)_3 + H^+ \qquad (2)$$

$$CH_3\overset{\overset{OH}{|}}{P}(OC_6H_5)_3 \overset{K_3}{\rightleftharpoons} CH_3\overset{\overset{O^-}{|}}{P}(OC_6H_5)_3 + H^+ \qquad (3)$$

$$CH_3\overset{\overset{O^-}{|}}{P}(OC_6H_5)_3 \xrightarrow{k_2} CH_3\overset{\overset{O}{\|}}{P}(OC_6H_5)_2 + C_6H_5O^- \qquad (4)$$

If the mechanism presented in Scheme I is correct, k_1 should control the rate-limiting addition of water in dilute acid solutions, whereas in more concentrated acid, k_2 should control the rate-limiting loss of phenoxide ion from the phosphorane anion. The mechanism predicts that, at high acidity, the rate of hydrolysis will be inversely as the second power of h_0; Figures 3 and 4 show the rate constants of hydrolysis as a function of acid concentration at two concentrations of water in acetonitrile. Although the h_0 function for these solvent mixtures is not yet known,[5] the data qualitatively support the mechanism here advanced; the predicted inhibition of the reaction by acid is observed.

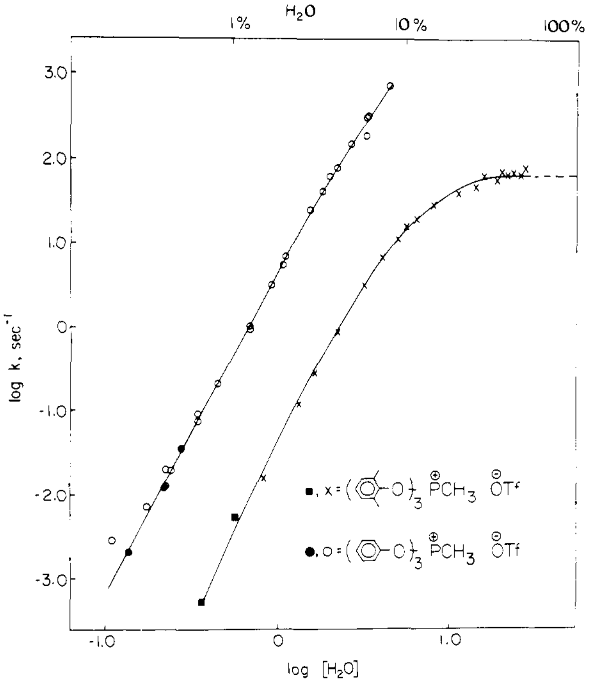


Figure 1. Rate constants in inverse seconds for the hydrolysis of methyltriphenoxyphosphonium triflate and of methyltri(2,6-dimethylphenoxy)phosphonium triflate, at 25°, plotted as a function of the concentration of water in acetonitrile as solvent. Open circles and X's: measurements with a Durham-Gibson stopped-flow apparatus; filled circles and squares: measurements with a Cary 15 spectrophotometer.