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PHOSPHATE MONOESTERS MONOANIONS AS PRECURSORS FOR METAPHOSPHATE ION STRUCTURAL MANIFESTATION IN THE SOLID STATE

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Abstract: Average molecular parameters of the phosphate group in phosphate monoesters monoanions, $ROPO_3H^-$ (1), obtained from twenty five structures reported in the literature, have been compared with those in phosphate triesters, (2) obtained from thirteen reported structures. Analysis of the P-O bond distances and OPO bond angles in these two systems leads to the conclusion that (1) shows structural features compatible with an "early stage" of the S_N1 fragmentation yielding alcohol ROH and PO_3^- ion.

The metaphosphate ion, PO_3^- was postulated thirty years ago[1] as a reactive intermediate involved in the hydrolysis of phosphate monoesters, and its existence in the monomeric form in the gas phase has recently been demonstrated by NICl mass spectrometry.[2] Participation of the metaphosphate type species attracts unceasing attention,[3] and recent reports[4] show that a variety of neutral, phosphorus-containing systems can function as precursors for the metaphosphate derivatives of the general formula $X\text{-}PO_2$. Theoretical calculations suggest[5] that it is not the intrinsic instability, but rather the high electrophilicity of the metaphosphate monomer that makes it such an elusive reaction intermediate. According to the original proposal,[1] it is the monoanion 1 of a monoester that represents the reactive form of a substrate. The rate-determining, unimolecular step involves the internal nucleophilic centre (ionized oxygen atom), as well as the acidic hydrogen which assists the departure of a leaving group; the molecule of water may or may not participate in the proton transfer.

$$\underset{1}{ROP(O)(OH)O^-(H_2O)} \longrightarrow ROH + PO_3^-(H_2O) \qquad (1)$$

These conditions for unimolecular fragmentation are also met in crystals of the salts of the phosphoric acid monoesters monoanions; intermolecular hydrogen bonding[6] providing the mechanism for the proton transfer required for the departure of the molecule of alcohol.

It therefore seemed worthwhile to search the available molecular parameters of ions of type 1 for any manifestation of structural features which would indicate that these ions act, even in the solid state, as precursors for the metaphosphate ion.[7] Since virtually all phosphate tetrahedra, PO_4 deviate significantly from the ideal tetrahedral geometry,[8] in order to obtain meaningful structural correlations for 1, an appropriate reference system had to be defined. Phosphoric triesters, $(RO)(R^1O)(R^{11}O)PO$, 2 have been chosen as the reference, and since esters 2 undergo nucleophilic cleavage *via* the associative, not dissociative mechanism,[9] the molecular parameters of 2 have been taken as "typical" for a "low reactivity" phosphate ester group.

Crystal structures of twenty five salts 1 and thirteen triesters 2 have been reported in the literature;[10] the calculated average phosphorus-oxygen distances for individual types of P-O bonds in these two systems are given in the Table.

Table. Average P-O bond lengths (Å) for phosphates 1 and 2 (s.d. in parenthesis)

	P-OR	P-OH	$P-O^-$	P=O
1	1.61(2)	1.55(2)	1.51(1)	1.49(1)
2	1.56(1)			1.44(1)

It can be seen from the Table that the four P-O bonds in 1 are different, *i.e.* the negative charge is not symmetrically distributed between the two oxygens of the PO_2^- group.[11] The characteristic feature of the P-O bonds in 1 is the unusually large (and constant) phosphorus-oxygen (ester) bond distance, as compared with the same bond in a triester system. It is interesting to note that in the triesters containing an ester group derived from strongly acidic precursor ($pK_a < 5$), the P-OR bond distance reached the limiting value of *ca.* 1.60 Å.[14] These bonds were therefore considered as "atypical" of an ester group and were not included in the calculation of the average P-OR bond distance in 2. In monoesters 1, on the other hand, the "long" P-OR bonds (1.61 ± 0.02Å) were found irrespective of the nature of the R group; in fact in all but two cases, the RO groups were derived from aliphatic alcohols, *i.e.* intrinsically poor leaving groups. The observed lengthening of the P-O (ester) bond in 1 relative to that in 2 can be taken as a measure of the advancement of 1 along the reaction coordinate in a S_N1 process. If this increment in bond distance is related to the bond number, n_{PO}, according to Pauling's equation: $\Delta r_i = -c \log n_i$, where c = 0.47 for P-O bonds,[7] the value of $n_{PO} = 0.78$ is obtained for 1. This can be interpreted as indicating that the P-O (ester) strength in all twenty five salts 1 studied has been reduced to a constant value of *ca.* 78% of that for the same bond in a triester molecule.

The P-OR distance changes that occur during the fragmentation of 1 are paralleled by changes of the bond angles at phosphorus. As the reaction progresses, the three RO-P-O angles tend towards 90°, while the remaining three O-P-O angles should approach the 120° expected for a trigonal PO_3^- ion. In agreement with this requirement, the average value for the RO-P-O angle in phosphate monoesters monoanions was found to be rather small and constant (106.3 ± 0.5°); the remaining O-P-O angles give the average value of 112.1 + 4.0°. Assuming that the bond-number conservation postulate[15] holds for system 1, and that 1 shows approximate C_{3v} symmetry, the bond number n_{PO} can be correlated[16] with the average value of the angle θ between the bond in question and the remaining three bonds at the tetrahedral center by the equation: $n_i = 9\cos^2\theta$. According to this relationship, $n_{PO} = 0.71$, thus confirming the result obtained from the analysis of the P-OR distance. It can be concluded that the molecular parameters of the phosphate group in salts 1, when compared with those of triesters 2, indicate up to a 20-30% advancement towards fragmentation products.

The characteristics of the phosphoryl bond in 1 support the conclusion that the monoesters monoanions can serve as models for an "early stage" of the fragmentation reaction. The typical length for the P=O bond in organophosphorus compounds is 1.45 Å;[17] the analysis of crystal structures of ten phosphoric diesters anions, $(RO)_2PO_2^-$ showed that the introduction of a negative charge results in an increase of the P=O bond distance to an average value of 1.47 ± 0.01 Å. The phosphorus-oxygen distance in the P=O group in 1 is even longer than that (see Table), and we interpret this result in terms of the partial "metaphosphate-like" character of the PO_3 group in 1. Although the molecular parameters for the free metaphosphate ion are not experimentally accessible, *ab initio* calculations[5] on the PO_3^- ion showed that the effect of d orbitals on bonding give a P-O bond distance of as much as 1.54 Å.

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