

chromatography on basic alumina using carbon tetrachloride as eluent. A quantity of 1.3 g of compound (mp 38–39 °C) was obtained which crystallized on cooling after the eluent had been evaporated. Its ¹H and ¹³C NMR spectra (Tables I and II) and its high-resolution mass spectrum confirmed its identity as **10**.

Anal. Calcd for C₁₀H₁₂O₃: mol wt, 180.0786. Found (mass spectrum at 70 eV): mol wt, 180.0781.

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Electron-Impact and Field-Ionization Mass Spectrometry of α -Ketol Phosphate Salts. Gas-Phase Thermolysis of Phosphodiester to Monomeric Alkyl Metaphosphate. Appearance and Origins of Original Salt Cations in Mass Spectra

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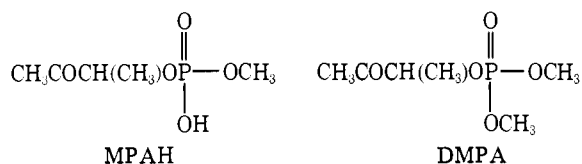
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Abstract: The electron-impact (EI) and field-ionization (FI) mass spectra of two salts derived from α -ketol phosphates, 1-methyl-3-carbamylpyridinium 3-oxo-2-butyl phosphate and 1-methyl-3-carbamylpyridinium methyl(3-oxo-2-butyl) phosphate, have been measured. These salts undergo the expected facile thermal transmethylation to nicotinamide and the corresponding phosphodiester and -triester, methyl(3-oxo-2-butyl) phosphate and dimethyl(3-oxo-2-butyl) phosphate, respectively. The diester, but not the triester, undergoes further thermal decomposition to 3-oxo-2-butanol and presumably monomeric methyl metaphosphate, CH₃OPO₂. In addition, the EI and FI spectra obtained from the salts contain peaks at the mass of the original salt cation and a mass one unit greater. In the FI spectra, however, they are accompanied by arrays of additional peaks at precisely those mass numbers that one would expect to observe in field-desorption (FD) spectra of the salts, and which we interpret as a FD component in the nominally FI spectra. The data thus suggest that the salt is in thermodynamic equilibrium with an isomeric covalently bound molecule, which volatilizes and travels the ca. 1 cm from probe to anode via the gas phase, is adsorbed on the anode, reverts to the original salt, and undergoes conventional FD. This and analogous covalent intermediates are most probably the source also of the "salt cation" peaks in the EI spectra of these salts and of others reported in the literature—cinnolinium, tropylium, pyrylium, and 1,2-dithiolylium salts and the cationic dye crystal violet.

The original intent of this work was to examine the behavior in the mass spectrometer of diesters and triesters derived from α -ketol phosphates, that is, simple analogues of the sugar

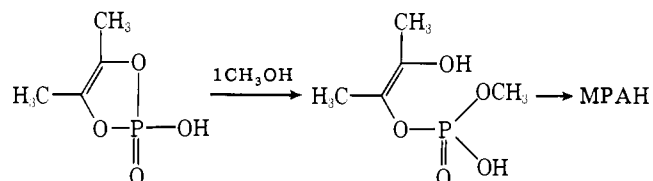
phosphates.² Our main objective was to search for evidence of monomeric metaphosphate intermediates, ROPO₂, in ionic or intervening thermal³ reactions of derivatives of acetoin

(3-oxo-2-butanol).⁴ Monomeric methyl metaphosphate, CH_3OPO_2 , has recently been reported to be formed by py-



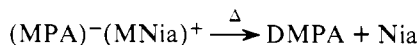
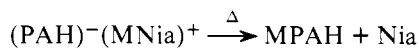
rolysis of 2-methoxy-2-oxo-2*H*-1,2-oxaphosphorinene-4 at 600 °C.⁵ The pyrolysis results have been offered in support of the hypothesis that monomeric metaphosphate species are formed as intermediates in hydrolysis, and in other phosphoryl-transfer reactions, of certain derivatives of phosphoric acid.⁵ In its original conception,⁶ the monomeric metaphosphate hypothesis referred to the hydrolysis of phosphomonoesters in aqueous solution; however, broader applications of the hypothesis have also been suggested,⁷ and recently evidence has been offered on the trapping of metaphosphate species in a three-phase system consisting of two polymers and one nonaqueous solution.⁸ Thermodynamic considerations dealing with the dehydration of orthophosphoric acid to metaphosphoric acid^{9a} and a molecular-orbital study of monomeric metaphosphate^{9b} have been published recently.

An obvious route to the diester, MPAH, appeared to be the reaction of methanol with 4,5-dimethyl-2-hydroxy-2-oxo-2*H*-1,3,2-dioxaphospholene.¹⁰ However, preliminary inves-



tigation disclosed that the product of this reaction volatilized in the mass spectrometer as a dimer, $(\text{MPAH})_2$, of the desired molecule, and the approach was therefore unsuitable for our purpose.

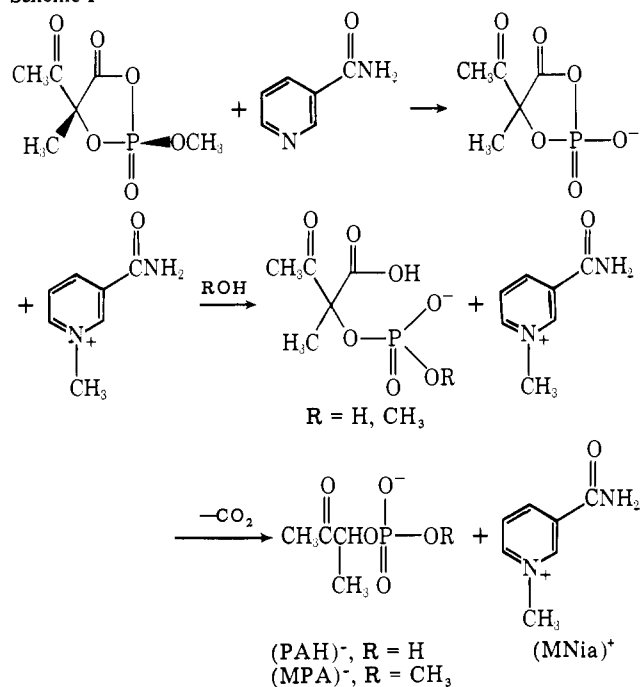
Another reaction capable of producing the desired phosphate esters, shown in Scheme I, proceeds from 5*r*-acetyl-2*r*-methoxy-5*c*-methyl-2,4-dioxo-2*H*-1,3,2-dioxaphospholane.¹¹ Reaction of the intermediate cyclic acyl phosphate aminium salt with water and with methanol, respectively, is known to yield the corresponding salts of the phosphomonoester, $(\text{PAH})^-(\text{MNia})^+$, and phosphodiester, $(\text{MPA})^-(\text{MNia})^+$.¹¹ Thermal transmethylation in these salts should occur easily in the mass spectrometer to generate the desired diester and triester in situ, accompanied by nicotinamide:



We used direct-probe injection of the salts into the ionization chamber and measured both EI and FI mass spectra. This approach provided an opportunity to examine the results of thermal and EI-induced reactions of the esters in the gas phase and also, as described below, to observe some unanticipated behavior of the salts as well.

EI mass spectra of *N*-methylpyridinium perchlorates and iodides and related salts have been reported.¹² Like aliphatic quaternary ammonium salts,¹³ they do not volatilize intact but undergo thermal reactions to produce volatile species, which are observed in the mass spectra. Spectra obtained from certain cinnolinium,¹⁴ tropylium,¹⁵ pyrylium,¹⁶ and 1,2-dithiolylium¹⁷ salts show intense peaks at the masses of the original cations, which are thought to undergo thermal reduction to the free radicals; the latter, in turn, volatilize and are observed in the

Scheme I



spectra. Crystal violet, a cationic dye, is reported to give intense peaks at masses 372 and 373, where 372 = mass of the original cation; these peaks are attributed to the volatile leuco crystal violet, postulated to be formed also by thermal reduction of the original sample on the heated sample probe.¹⁸ Brent and his associates¹⁹ have circumvented the intervening thermal reactions of a series of aliphatic quaternary ammonium tosylates and halides by the new technique of FD mass spectrometry,²⁰ in which a preformed positive ion is thought to be driven from the emitter (anode) surface into the gas phase. The most intense peak in each of the five FD spectra they reported occurs at the mass of the original cation, and three of the spectra show a peak of moderate intensity at a mass equal to that of a complex of two cations and one anion. Counterparts of such a complex, which may be viewed as a solvated cation where the solvating "molecule" comprises one unit each of the original cation and anion, are prominent in the FD spectra of sodium acetate,²¹ potassium guaiacolsulfonate,²² sodium benzenesulfonate,²³ sodium salts of diethyl stilbestrol glucuronide and bile acids,²⁴ a series of phosphonium halides,²⁵ trimethylsulfonium iodide,²⁶ triethyloxonium hexafluorophosphate,²⁶ and several cationic and anionic dyes.¹⁸ At various anode heating currents, sodium benzenesulfonate gave substantial yields also of complexes consisting of Na^+ and two, three, four, and five molecules, in accord with the view that such cluster ions are solvated cations.²³ The most intense peak in the FD mass spectrum of each of six reported phosphonium halides at relatively low anode heating current corresponds to the original quaternary phosphonium ion,²⁵ paralleling the behavior of the quaternary ammonium salts reported by Brent.¹⁹ In an extension of Brent's approach, Veith has recently reported the original cation and a series of complexes of one cation with one to as many as five molecules in the FD spectra of some 20 quaternary ammonium and carbenium salts.²⁷

Mass spectra of alkyl phosphates,²⁸ phosphites,²⁹ and phosphonates³⁰ have long been known to contain ions with elemental compositions that can be construed as the protonated monomeric metaphosphoric acid and alkyl metaphosphate structures, $(\text{HPO}_3)\text{H}^+$ and $(\text{RPO}_3)\text{H}^+$, where $\text{R} = \text{CH}_3$ and C_2H_5 , although the actual structures of such ions are not certain. Analogous protonated species—methyl metathio-phosphate, phenyl metaphosphate, metaphosphoramidate, meta-

phosphoramidates, and further derivatives—have more recently been observed in the mass spectra of trimethyl thio- and dithiophosphates,³¹ dimethyl and diethyl vinyl (and substituted vinyl) phosphates,^{32,33} 5,5-dimethyl-2-oxo-2-R-1,3,2-dioxaphosphorinane, where R = OCH₃, OC₆H₅, SCH₃, and N(CH₃)₂,³⁴ and several phosphoramidates,^{35,36} phosphonates,³⁷ and phosphonoamidates.³⁷

Neutral molecules with compositions corresponding to metaphosphoric acid, phenyl metaphosphate, metaphosphoramidate, metaphosphoryl chloride, and *N,N*-dimethylmetaphosphoramidate, respectively, are apparently eliminated in decompositions induced by EI on bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl),³⁸ diphenyl triphenylphosphoranylidene-methyl- and -ethylphosphonates,³⁹ dibenzyl and diphenyl phosphoramidates,³⁵ and tetrahydropyrano[2,3-*e*]-2-thio-2-chloro-⁴⁰ and 2-dimethylamino-1,3,2-dioxaphosphorinanes.⁴⁰ Finally, FD mass spectra of adenosine 5'-monophosphate,⁴¹ pyridoxamine 5'-phosphate,⁴² and pyridoxal 5'-phosphate⁴² show clearly the loss of the elements of neutral metaphosphoric acid, although the order of events—whether the elimination precedes or follows ionization—is not known.⁴³

None of the mass spectral studies cited above makes explicit reference to protonated or neutral monomeric metaphosphate structures in connection with the reported observations. Moreover, the mass spectral data bearing on the possible generation of metaphosphate species have not been noted in any of the reports dealing with monomeric metaphosphate in hydrolysis of phosphates^{6,8} or pyrolysis of phosphonates.⁵

Phosphoryl-transfer reactions of phosphotriesters, (RO)₃PO, and analogous compounds, XP(O)(OR)₂, where the simple elimination of metaphosphate does not come into play are now regarded as proceeding via oxyphosphoranes.⁴⁴ Evidence for the participation of hexacoordinate phosphorus intermediates in nucleophilic catalysis of phosphorylations by cyclic and acyclic phosphotriesters in aprotic solvents has recently been offered: P(4) → P(5) → P(6) → P(5) → P(4).⁴⁵ With respect to nucleophilic substitutions at the phosphorus of phosphodiester, (RO)₂P(O)OH, and related compounds, XP(O)(OR)(OH), the prevailing view seems to be that these reactions occur via an addition-elimination (oxyphosphorane) mechanism, rather than via an elimination-addition (alkyl metaphosphate) mechanism.

Experimental Section

Preparation of 1-Methyl-3-carbamylpyridinium 3-Oxo-2-butyl Phosphate, (PAH)⁻(MNia)⁺, and of 1-Methyl-3-carbamylpyridinium Methyl(3-oxo-2-butyl) Phosphate, (MPA)⁻(MNia)⁺. *5*r**-Acetyl-2*r*-methoxy-5*c*-methyl-2,4-dioxo-2*H*-1,3,2-dioxaphospholane was prepared as described,¹¹ and was utilized in the next two reactions.

A. A mixture of the cyclic triester (8.69 g, 41.7 mmol) and nicotinamide (5.11 g, 41.7 mmol) in anhydrous benzene (20 mL) was kept for 15 min at reflux temperature, and was cooled to 0 °C. The benzene was decanted, and the insoluble cyclic salt was repeatedly washed with anhydrous benzene. The salt was mixed with anhydrous acetonitrile (20 mL), cooled to 0 °C, and treated with water (0.75 g, 41.7 mmol). After a few minutes, the solution was evaporated under vacuum, and the remaining acyclic salt, (PAH)⁻(MNia)⁺, was examined by mass spectrometry; its ¹H and ³¹P NMR spectral properties agreed with those previously reported.¹¹

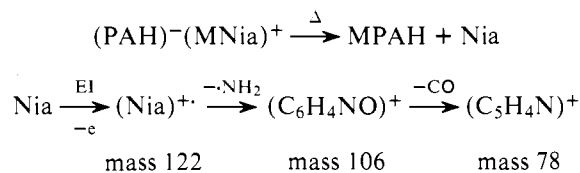
B. The cyclic triester and nicotinamide were allowed to react as described in A, and the resulting cyclic salt was mixed with anhydrous dichloromethane. This mixture (at 0 °C) was treated with 1 molar equiv of anhydrous methanol, and the solution was evaporated under vacuum to yield the acyclic salt, (MPA)⁻(MNia)⁺, which was examined by mass spectrometry. The ¹H and ³¹P NMR spectral data agreed with those in the literature.¹¹

Mass Spectrometry of the Salts. Analogue spectra, at a resolution of about 3000, were measured on a CEC Model 21-110B instrument, with sample injection via probe. To minimize exposure to atmospheric oxygen and water, each sample was transferred from the glass vial in

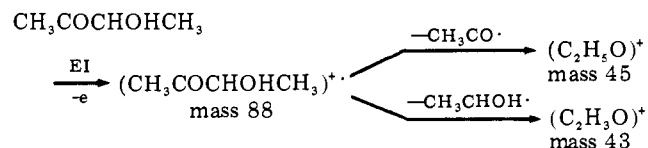
which it had been stored to the probe tube under a blanket of nitrogen and frozen in liquid nitrogen, and the probe was then quickly introduced into the instrument vacuum system and pumped down. In every case, a series of spectra was recorded as the source temperature was raised from an initial value of about 80–100 °C to a final value of 300–400 °C. No heat was applied directly to the probe, which, however, was in thermal contact with the ion source. The sample temperature under these conditions follows the source temperature, but how closely it follows is uncertain; the extent of the lag may be considerable. EI spectra were measured with 70-eV electrons. FI operation employed a Schick uncoated stainless steel blade⁴⁶ as the emitter, as recommended by Derrick et al.,⁴⁷ lightly conditioned in the spectrometer with benzonitrile for 30 min while the source temperature was gradually reduced from an initial value of about 225 °C to about 125 °C. Anode and slit voltages during both conditioning and recording of spectra were +8 and -2.2 kV, respectively. Spacing between the blade and slit was 0.020 in.

Results

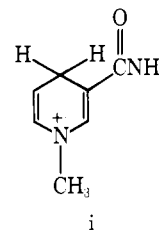
EI Spectra. A. Phosphomonoester Salt, (PAH)⁻(MNia)⁺. At the lowest source temperatures employed, 102–108 and 120–134 °C,⁴⁸ the spectra show only the set of ions associated with nicotinamide (Nia), which undoubtedly arises by thermal transmethylation:



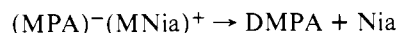
At increasing temperatures, 152–175 and 198–224 °C, the well-defined, although weak, mass-deficient⁴⁹ peak corresponding to the molecular ion of the phosphodiester, (MPAH)⁺, is observed at mass 182, accompanied by several mass-deficient peaks at nominal masses characteristic of alkyl phosphate fragment ions,^{28,33,50} and by intense peaks at masses 88, 45, and 43, the latter group strongly suggesting aceto-



The spectra also contain peaks at the mass of the cation of the original salt, (MNia)⁺, 137, and at a mass one unit higher, (MNiaH)⁺. The latter can be represented tentatively as the reduced radical cation i or its ortho-hydrogenated isomer.



B. Phosphodiester Salt, (MPA)⁻(MNia)⁺. At the lowest source temperature employed, 108–110 °C, the spectrum shows nicotinamide, again attributed to thermal transmethylation:



and a weak peak at the mass of the cation of the salt, (MNia)⁺. At higher temperatures, 130–148 and 170–178 °C, the spectra show a well-defined mass-deficient peak for the molecular ion of the triester, (DMPA)⁺, at mass 196; mass-deficient phosphorus-containing fragment-ion peaks commonly observed in the spectra of alkyl phosphates; and weak peaks for (MNia)⁺

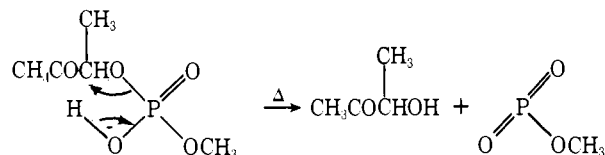
and $(\text{MNiaH})^+$. In contrast to the spectra of the phospho- monoester salt, the spectra of this salt show no evidence for acetoin.

FI Spectra. The "optimum" FI spectra are displayed in Table I, which includes all peaks with intensities $\geq 1\%$ that of the most intense peak. At higher temperatures the spectra of the two salts show greatly increased numbers of peaks extending to higher masses, presumably reflecting thermal reactions. Among the prominent features of all the spectra at higher temperatures are peaks attributed to nicotinonitrile, the known thermal dehydration product of nicotinamide.⁵²

The ion of mass 137, which is relatively abundant in the FI spectra of both salts, is attributed to the 1-methylnicotinamide ion. Other ions in Table I correspond to the MNia^+ ion "solvated" by molecules of Nia (masses 259, 381) or of both Nia and the entire salt "molecule" (mass 563). Protonation of salt anions occurs frequently, either without associated fragmentation, in which case there may or may not be further "solvation" (masses 183, 306, 319, 549), or with fragmentation, in which case there seems generally to be no association with additional polyatomic entities other than an original salt cation (masses 139, 152, 153, 262, 263, 276, 277).

The FI spectra at temperatures lower than those shown in Table I are simpler. Thus, the monoester salt at 78–86 and 94–98 °C shows clearly only peaks for Nia^+ and $(\text{Nia})_n\text{H}^+$, where $n = 1-5$; the diester salt at 108–110 and 120–134 °C, similarly, gives chiefly Nia^+ and $(\text{Nia})_n\text{H}^+$, $n = 1,2$. The range of values of n is highly sensitive to source temperature and is not significant for our purposes.

The acetoin observed in the EI spectra of only the phospho- monoester salt is most readily accounted for as a thermal decomposition product of the ester, in which case it should



appear also in the FI spectra. We detected neither the radical cation $\text{C}_4\text{H}_8\text{O}_2^+$ of mass 88 nor the protonated molecule $\text{C}_4\text{H}_9\text{O}_2^+$ of mass 89. However, the FI spectra measured at source temperatures of 218–250, 258–288, 294–310, and 332–350 °C all show an intense peak at mass 177, probably attributable to $(\text{C}_4\text{H}_8\text{O}_2)_2\text{H}^+$, which can be viewed as a proton-bound dimer or a proton solvated by two molecules of acetoin. Further tentative evidence for acetoin is found in an intense peak at mass 211 in the second, third, and fourth of these spectra and another at mass 225 in the third and fourth. Suggested assignments of these peaks are $(\text{C}_4\text{H}_8\text{O}_2)(\text{NiaH})^+$ and $(\text{C}_4\text{H}_8\text{O}_2)(\text{MNia})^+$, respectively. This group of peaks attains maximum intensities in the same range of source temperatures, about 200–300 °C, as the peaks attributed to acetoin in the EI spectra. The corresponding FI spectra obtained from the phosphodiester salt show only very weak peaks at these masses, suggesting no more than a possible trace of acetoin, and they show no evidence for 3-methoxy-2-butanone, a conceivable product from the analogous reaction involving methyl migration. The mutual consistency of the EI and FI spectra and the contrasting indications for the two compounds, taken together, thus support the suggestion that acetoin arises by a thermal intramolecular elimination as shown. We found no direct evidence for the ionized $(\text{CH}_3\text{OPO}_2)^+$ in either EI or FI spectra, but peaks derived from this species could well be obscured by other components.

Discussion

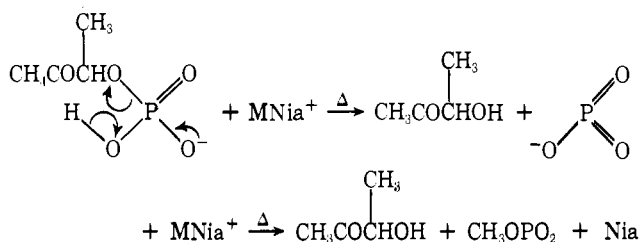
We considered an elimination reaction in the original salt anion as a possible alternative path leading to acetoin and

Table I. Field Ionization Mass Spectra

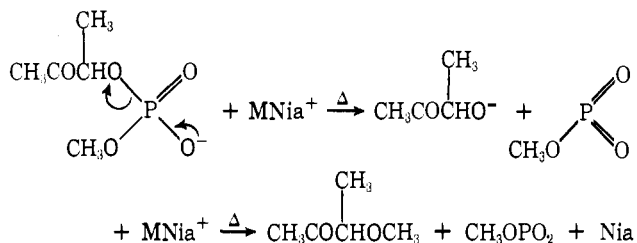
Compd	$(\text{PAH})^-$ $(\text{MNia})^+$	$(\text{MPA})^-$ $(\text{MNia})^+$	
Source temp, °C	132–146	172–192	
Mass	Intensity	Intensity	Suggested assignment
105		11	$\text{NiaH}^+ - \text{H}_2\text{O}$
119 ^b		2	$\text{MNia}^+ - \text{H}_2\text{O}$
120 ^b		13	$(\text{MNiaH})^+ - \text{H}_2\text{O}$
121		2	
122	6	24	$(\text{Nia})^+$
123	23	100	$(\text{NiaH})^+$
124	1	8	<i>a</i>
137 ^b	38	34	$(\text{MNia})^+$
138 ^b	9	17	$(\text{MNiaH})^+$
139 ^b	3	33	$(\text{MPAH})\text{H}^+ - \text{CH}_3\text{CHO}$
140 ^b	4	4	$(\text{MPAH})\text{H}^+ - \text{CH}_3\text{CO}$
141	2	3	
152 ^b	3	3	$(\text{MPAH})\text{H}^+ - \text{CH}_3\text{O}$
153 ^b	3	9	$(\text{MPAH})\text{H}^+ - \text{CH}_2\text{O}$
154		1	
183 ^b		7	$(\text{MPAH})\text{H}^+$
189		2	
190		2	
191		2	
192		2	
193		2	
197		3	$(\text{DMPA})\text{H}^+$
210		2	
219		1	
237		1	
243		2	
244	3	1	
245	100	13	$(\text{Nia})_2\text{H}^+$
246	19	2	<i>a</i>
247	1		<i>a</i>
259 ^b	14		$(\text{Nia})(\text{MNia})^+$
260 ^b	7		$(\text{Nia})(\text{MNiaH})^+$
261 ^b	3	3	$(\text{MPAH})(\text{NiaH})\text{H}^+ - \text{CH}_3\text{CHO}$
262 ^b	5		$(\text{PAH})(\text{MNia})\text{H}^+ - \text{CH}_3\text{CO}$
263 ^b	3		$(\text{PAH})(\text{MNia})\text{H}^+ - \text{CH}_2\text{CO}$
276 ^b		1	$(\text{MPA})(\text{MNia})\text{H}^+ - \text{CH}_3\text{CO}$
277 ^b		1	$(\text{MPA})(\text{MNia})\text{H}^+ - \text{CH}_2\text{CO}$
305 ^b		10	$(\text{MPAH})(\text{NiaH})^+$
306 ^b		10	$(\text{MPAH})(\text{NiaH})\text{H}^+$
307		2	<i>a</i>
319 ^b		8	$(\text{MPA})(\text{MNia})\text{H}^+$
320 ^b		2	$(\text{MPAH})(\text{MNia})\text{H}^+, ^a$
321		2	
349		1	$(\text{Nia})_3\text{H}^+ - \text{H}_2\text{O}$
365		1	
366	1		
367	32	1	$(\text{Nia})_3\text{H}^+$
368	6		<i>a</i>
369	1		<i>a</i>
381 ^b	2		$(\text{Nia})_2(\text{MNia})^+$
405	1		
406	3		
436	1		
469		2	$(\text{Nia})_4\text{H}^+ - \text{H}_2 - \text{H}_2\text{O}$
489	3		$(\text{Nia})_4\text{H}^+$
490	2		$(\text{Nia})_3(\text{NiaH})\text{H}^+$
549 ^b	10		$(\text{PAH})(\text{MNia})(\text{Nia})_2\text{H}^+$
550	3		<i>a</i>
563 ^b	3		$(\text{PAH})(\text{MNia})_2(\text{Nia})^+$
564	1		<i>a</i>
611	5		$(\text{Nia})_5\text{H}^+$
612	2		<i>a</i>

^a Peaks attributed to naturally occurring heavy-isotopic species.

^b Peaks attributed to field desorption of the original salt.



methyl metaphosphate. If this is a viable alternative, however, one would expect that the phosphodiester salt anion should undergo a similar reaction except that, in the absence of a hydrogen atom accessible for migration within the anion, it should lead to the methyl ether of acetoin in place of acetoin itself. Our failure to find any evidence for the methyl ether

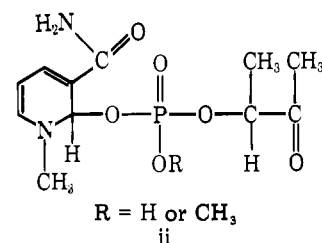


makes this alternative appear improbable. The orthophosphate monoanion, in the capacity of reactant species, plays a central role in the original metaphosphate hypothesis,⁶ but the postulated reaction requires the participation of a water molecule as well, and in this respect the hydrolysis and the pyrolysis reactions differ significantly.

The combined EI and FI data strongly suggest that the α -ketol phosphodiester MPAH, but not the triester DMPA, generates monomeric methyl metaphosphate in a thermal process in the gas phase. This finding, the literature report⁵ of a gas-phase pyrolytic formation of monomeric methyl metaphosphate under conditions far more drastic than obtained in our work, and the large amount of pertinent mass spectral data,²⁸⁻⁴³ taken together, constitute compelling evidence for the existence of monomeric metaphosphate⁷ species. Having come this far, however, we must confess that this conclusion appears to us to have no necessary bearing on the question of whether monomeric metaphosphate species are generated in the hydrolysis of phosphate esters, or in any other phosphoryl transfer in aqueous or nonaqueous solutions. Indeed, one could argue that, since the hydrolysis of phosphodiester is thought to take place via oxyphosphoranes rather than via alkyl metaphosphates, the appearance of the latter species in gas-phase pyrolysis of a phosphodiester speaks against any more specific correlation between gas-phase and solution reaction mechanisms in phosphate esters in general.

A totally unforeseen finding of the present investigation, the occurrence in the FI spectra of both salts, $(\text{PAH})^-(\text{MNi}^+)$ and $(\text{MPA})^-(\text{MNi}^+)$, of ionic species apparently incorporating the original anion, cation, or both, suggests processes usually associated with FD mass spectra of organic salts. Several of these species are formulated as solvated cations. The physicochemical processes comprising field desorption are recognized as occurring also in the usual course of FI mass spectrometry, but the molecules involved must first travel via the gas phase from the probe to the anode, a distance of about 1 cm, before they can be adsorbed and then undergo ionization and reenter the gas phase.^{20,53} The clear implication is that the salts under study in this work volatilize intact to an extent sufficient to produce an appreciable FD component in the FI mass spectra. The (MNi^+) and $(\text{MNi}^+\text{H})^+$ ions observed in the EI spectra most probably stem also from salt "molecules" that volatilize intact, rather than, or in addition to, thermally reduced neutral species formed on the heated probe.¹⁴⁻¹⁸

Mass spectra of many classes of internally charged molecules have been reported,⁵⁴ and even when ionized by 70-eV electrons they generally yield intense peaks for the molecular ion. In such species, in contrast to salts, the positively and negatively charged centers are held together by covalent bonds, which would seem to be essential for volatilization as an intact molecule. A recent report that tropylium isothiocyanate exists as an equilibrium mixture of covalent and ionic species⁵⁵ suggests that such a molecule might volatilize intact and yield a molecular-ion peak in its mass spectrum. *N,N,N*-Trimethylanilinium oxides have been shown to volatilize intact, with the extent of accompanying conversion to nonmesoionic isomers determined by temperature and by steric and electronic effects.⁵⁶ Very recent reports have described ingenious new techniques for volatilizing salts and other "nonvolatile" and/or thermally fragile species with little or no prior thermal decomposition, thus allowing measurement of valid EI or chemical ionization mass spectra.⁵⁷ Our evidence, obtained without the help of such special techniques, that the two *N*-alkylpyridinium salts volatilize intact suggests a tight ion pair or, more likely, a covalently bound molecule where the separate charge centers do not persist:



or the 4- or 6-substituted isomer. In the course of the FI work, such a species presumably reverts to the original salt on the surface of the anode and then undergoes FD via physicochemical processes characteristic of salts.

Our combined EI and FI results on $(\text{PAH})^-(\text{MNi}^+)$ and $(\text{MPA})^-(\text{MNi}^+)$ can perhaps furnish a more explicit and, generally, more satisfactory model than the vaguely defined "thermal reductions" of salt cations that have been proposed to account for peaks in EI spectra at the masses of the original cations¹⁴⁻¹⁷ and, in some cases, at a mass 1 u greater.^{14,18} The sequence of events is most probably initiated by reorganization of the salt to a covalently bound molecule with which it is presumably in thermodynamic equilibrium. This molecule volatilizes and thus becomes subject to ionization/dissociation by EI, which can account reasonably and most simply for the observed "salt cation" peaks. Possible intervention of thermolytic reactions of the covalent intermediate might provide additional paths to regenerated salt cation and also, as suggested by a referee, to acetoin and a monomeric metaphosphate ester.

The state of the art in the area with which we have here been concerned is perhaps best summarized by juxtaposing the closing remarks from two review papers of a few years back, both concerned with the chemistry of phosphate esters and related species. "In summary, the chemistry of phosphorus and especially phosphate is relatively well understood. Basic principles have been established in describing the mechanistic behavior of phosphate in chemical systems . . .",⁵⁸ On the other hand, "There are many unanswered questions in a field in which little is known with certainty and almost all is conjecture".⁵⁹

References and Notes

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- (3) The term "thermal" will be used here to denote reactions preceding ionization.
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