(1969); (c) E. J. Corey and J. I. Shulman, *J. Am. Chem. Soc.*, **92**, 5522 (1970); (d) K. Oshima, H. Takahashi, H. Yamamoto, and H. Nozaki, *ibid.*, **95**, 2693 (1973); (e) K. Oshima, H. Yamamoto, and H. Nozaki, *ibid.*, **95**, 4446 (1973); (f) H. Takahashi, K. Oshima, H. Yamamoto, and H. Nozaki, *ibid.*, **95**, 5803 (1973); (g) L. Brandsma and H. D. Verkruijsse, *Recl. Trav. Chim. Pays-Bas*, **93**, 319 (1974); (h) S. Takano, M. Hirama, T. Araki, and K. Ogasawara, *J. Am. Chem. Soc.*, **98**, 7084 (1976); (i) S. Takano, E. Yoshida, M. Hirama, and K. Ogasawara, *J. Chem. Soc., Chem. Commun.*, 776 (1976); (j) R. Gompper and W.-R. Ulrich, *Angew. Chem.*, **88**, 300 (1976).

(4) For amino-Claisen rearrangement, see (a) P. S. Mariano, D. Dunaway-Mariano, P. L. Huesmann, and R. Beamer, *Tetrahedron Lett.*, 4299 (1977); (b) P. S. Mariano, D. Dunaway-Mariano, and P. L. Huesmann, *J. Org. Chem.*, **44**, 124 (1979), and references cited therein.

(5) Y. Tamaru, T. Harada, and Z. Yoshida, *Tetrahedron Lett.*, 2169 (1978).

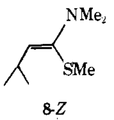
(6) J. Apsimon, "The Total Synthesis of Natural Products", Vol. 2, Wiley, New York, 1973.

(7) Conversion of thioamides to esters, ketene *S,S*-acetals, and dihydro-1,3-oxazines will be reported in the near future.

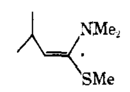
(8) (a) Y. Tamaru, T. Harada, and Z. Yoshida, *J. Am. Chem. Soc.*, **100**, 1923 (1978); (b) Y. Tamaru, T. Harada, H. Iwamoto, and Z. Yoshida, *ibid.*, **100**, 5221 (1978); (c) Y. Tamaru, T. Harada, and Z. Yoshida, *ibid.*, **101**, 1316 (1979).

(9) For ketene *S,N*-acetal formation under similar conditions, see R. Gompper and W. Elser, "Organic Syntheses", Collect. Vol. V, Wiley, New York, 1973, p 780.

(10) The following observation suggests that **3**-*Z* and **3**-*E* equilibrate under the reaction conditions, i.e., the ratio of a mixture of ketene *S,N*-acetals (**8**-



8-*Z*



8-*E*

E:**8**-*Z* = 6:4), which were generated by the treatment of *N,N*-dimethylthioisovaleroamide with methyl iodide and then with DBU in *tert*-butyl alcohol and distilled carefuly without adopting external heating and contaminated by *tert*-butyl alcohol, changed to a ratio of >9:<1 during storage overnight at an ambient temperature, as observed by ^{1}H NMR spectroscopy. This isomerization may be caused by *tert*-butyl alcohol, whose hydroxyl proton is acidic enough for the protonation of the highly nucleophilic double bonds of ketene *S,N*-acetals [cf. R. Gompper and W. Elser, *Justus Liebigs Ann. Chem.*, **725**, 64 (1969), and ref 8a].

(11) **4e** was obtained as a diastereoisomeric mixture. Although the ratios of diastereomers (**4c** and **4h**) were not able to be determined owing to their poor separation in ^{1}H NMR and LC (high-performance liquid chromatography), the ratios are expected to be reflected in the product ratios of Cope rearrangement (ca. 4:1 for both cases).

(12) A. F. Thomas, *J. Am. Chem. Soc.*, **91**, 3281 (1969).

(13) R. J. Crawford, W. F. Erman, and C. D. Broaddus, *J. Am. Chem. Soc.*, **94**, 4298 (1972).

(14) (−)-(*E*)-Ethyl lanceolate, $[\alpha]^{30}{}_{D}$ −50° (*c* 0.38, EtOH).[13]

(15) (−)-(*Z*)-Ethyl lanceolate, $[\alpha]^{30}{}_{D}$ −49° (*c* 0.35, EtOH).[13]

(16) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, Oxford, 1969, p 184.

Mass Spectrometry of Phosphate Esters. Phosphoacetoin and Its Methyl Esters

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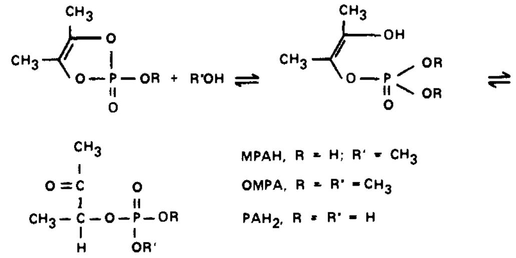
Abstract: The electron-impact (EI) and field-ionization (FI) mass spectra of 3-oxo-2-butyl phosphate (phosphoacetoin, PAH_2) and its mono- and dimethyl esters, MPAH and DMPA, all reveal additional components stemming from thermal reactions that occur both during sample storage and in the instrument. The acidic phosphates, PAH_2 and MPAH, break down thermally to acetoin and monomeric metaphosphoric acid or methyl metaphosphate, respectively. In addition, PAH_2 undergoes thermal dehydration to yield apparently a transient acetoin metaphosphate, which transforms rapidly to a cyclic enediol phosphate. Thermal disproportionation of MPAH into PAH_2 and DMPA takes place via a dimer formed by interaction of the acidic phosphoryl function with the carbonyl group; the neutral DMPA dimerizes by an aldol-type condensation. Ionic decomposition under EI is initiated, for the most part, by two primary processes: (a) loss of the acetyl radical and (b) hydrogen migration and loss of ketene. Process (a) is followed by loss, alternatively, of C_2H_2 or acetaldehyde; (b), by loss of C_2H_4, vinyl radical, or acetaldehyde. The hydrocarbon molecules so eliminated, C_2H_2 and C_2H_4, probably form initially as carbenes, $CH_2{=}C{:}$ and $CH_3CH{:}$, which presumably reorganize rapidly to acetylene and ethylene. A striking feature of the later stages of ionic decomposition of MPAH and DMPA is the loss of formaldehyde, apparently the preferred mode of disposing of methoxy groups in methyl esters of phosphoric and also phosphorous and related acids.

Introduction

The α-ketol phosphate function is present in important biological compounds, e.g., in dihydroxyacetone phosphate and its derivatives, which function as intermediates in gluconeogenesis and in the synthesis of phospholipids of biomembranes.[2] In addition, compounds of this type may be viewed as simple analogues of the sugar phosphates. A few attempts have been made to use mass spectrometry to study sugar phosphates but, without prior derivatization, the resulting spectra were so complex as to defy attempts to extract useful information from them.[3] Choosing to study a few simple α-ketol phosphates, we sought recently to examine the behavior in the mass spectrometer of two 3-oxo-2-butyl phosphates, methyl- (MPAH) and dimethylphosphoacetoins (DMPA), pictured in Scheme I.[4,5] Early in the study, we found that MPAH volatilizes in the spectrometer, at least in part, as dimer, prompting us to work instead with derived salts, from which the desired esters were then generated thermally in the ionization chamber. We have now returned to direct examination in the mass spectrometer of these phosphoesters and included the corresponding monoester, phosphoacetoin (PAH_2), and the related carboxylic ester, acetoin acetate, $CH_3CO_2CH(CH_3)COCH_3$, as well. We sought in this work to clarify the dimerization reaction(s) that

Scheme I



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intervened in our earlier investigation, to confirm our conclusion[5] that MPAH undergoes thermal decomposition to acetoin and monomeric methyl metaphosphate, to ascertain whether PAH_2 undergoes the analogous reaction to acetoin and metaphosphoric acid, and to provide further data that might contribute to a systematic treatment of the mass spectra of aliphatic phosphate esters.

The mass spectrometry of phosphate esters is the subject of an extensive literature.[5] Only a few publications, however, report enough spectra to serve as a basis for useful correlations or make any serious attempt to define the underlying chemistry. Thus, two reviews of the mass spectra of organophosphorus compounds, published in 1972[6] and 1976,[7] devote 2½ and less than 2 pages, respectively, to phosphate esters and list but a handful of literature references on this topic between them. The entire literature as of 1979 has little useful guidance to offer the would-be researcher in this area beyond what is available in three early papers: a preliminary glimpse of the mass spectrum of triethyl phosphate by McLafferty;[8] a survey of the major mass-spectral features and of inadvertent thermal[9] reactions of several trialkyl, triaryl, and mixed alkylaryl phosphates by Quayle;[10] and a careful study of the mass spectra of trimethyl and triethyl phosphates by Bafus, Gallegos, and Kiser.[11]

The work we report here has given us some insight into the reasons for the sparsity of systematic mass-spectral studies of phosphate esters, especially of alkyl phosphates. Two decades ago, Quayle noted the easy susceptibility of alkyl and alkylaryl phosphates to thermal decomposition, which, moreover, is catalyzed by free acids that result from the decomposition and deposit on the walls of the instrument.[10] Our data confirm this observation. Moreover, the spectra of acetoin phosphates are further complicated because of the reactivity of α-ketols and their derivatives. Thus, the recognition and clarification of inadvertent thermal reactions[9] were matters of continuous concern throughout this work.

A corollary effect, not mentioned by Quayle, consists of the efficient desorption by phosphoric acid of less polar wall deposits derived from previous samples over a time span of weeks, months, or years. The effect is reminiscent of an old "trick of the trade", the introduction into the spectrometer of a highly polar material such as concentrated ammonium hydroxide or methanol as a means of removing accumulated wall deposits.[12,13] For the most part, we abandoned the heated batch inlet system for sample introduction, going instead to direct probe injection into the ionization chamber, with temperature programming to vaporize the sample at the lowest feasible temperature. Even so, many of our spectra showed peaks at every mass number, detectable at higher temperatures to masses as high as 600–800, most of them due to hydrocarbon ions of indeterminate origins. To satisfy ourselves that we could distinguish with some measure of confidence between peaks stemming from such "garbage" and those due to the samples under study, we repeated the mass-spectral measurements many times over a 4-year period. Such differentiation was facilitated by the pronounced mass deficiency of phosphorus-containing ions relative to any plausible ions of the same nominal mass that contain solely carbon, hydrogen, and oxygen.[14] This same mass difference has served to flag peaks contributed by phosphorus-containing species in the mass spectra of pyrolysis products of flame-retardant cellulose.[15] It has also been exploited in using peaks due to phosphorus-containing ions as convenient internal mass markers for precise-mass measurements in pyrolysis/field-desorption mass spectrometry of deoxyribonucleic acid.[16]

The ionization/dissociation products reflected in mass spectra arise from a network of competing and consecutive reactions, and kinetic considerations associated with this network can account, qualitatively at least, for observed temperature effects[17] in the absence of intervening thermal reactions. If the sample is introduced via conventional heated batch inlet, the inlet is the most likely site for inadvertent thermal reactions, which can be detected in favorable cases by varying the inlet temperature or the time interval between introduction of the sample and measurement of the spectrum, and observing the ensuing spectral changes.[18-20] However, if the sample is introduced via probe directly into the ionization chamber, thermal reaction products more easily escape detection, especially if the peaks they contribute to the spectrum coincide with peaks that can be plausibly attributed to the original sample.[21] In the search for indications of thermal reaction products, we looked for individual peaks or groups of possibly related peaks that varied in intensity with temperature in a markedly different fashion than most of the peaks in the spectra, and we supplemented the EI spectra with mass spectra obtained by FI. The latter is a "softer" ionization process,[22] giving rise for the most part only to molecular ions, protonated molecules or monosolvated protons, more highly solvated protons, and fragment ions arising by low-energy processes, such as loss of H_2O from a solvated proton. In a few cases, as a further independent test of the origin of a radical cation that might have arisen either via a rearrangement/dissociation path from the molecular ion of the compound under study or by direct ionization of a thermal reaction product, we performed a metastable scan[23,24] of the questionable ion. Kinetic considerations dictate that ionic rearrangement reactions characterically give rise to intense metastable peaks;[25,26a] hence we took failure to find metastable peaks in such cases as evidence that the product arose by a thermal reaction.

Experimental Section

Preparation of PAH_2, MPAH, and DMPA. Water (0.19 g, 10.8 mmol), or methanol (0.20 g, 6.2 mmol), was added to a well-stirred suspension of 4,5-dimethyl-2-hydroxy-2-oxo-2*H*-1,3,2-dioxaphospholene[27] (1.613 g, 10.8 mmol, or 0.75 g, 5.0 mmol, respectively) in anhydrous diethyl ether (25 mL) or dichloromethane (10 mL), respectively, at 20 °C, with protection against moisture. After 10 or 45 min, respectively, the solution was evaporated at 20 °C, first at 30 mm, finally at 0.1 mm, until all solvent was removed. The IR and ^1H and ^{31}P NMR spectra of the PAH_2 and MPAH samples exhibited the expected signals,[28] and the samples were submitted to mass spectrometry without further purification.

Methanol (20 mL) was added to 4,5-dimethyl-2-methoxy-2-oxo-2*H*-1,3,2-dioxaphospholene[27] (7.05 g, 43 mmol) at 20 °C with stirring. After 30 min, the product was submitted to fractional distillation; the sample of DMPA submitted to mass spectrometry had bp 70 °C (0.05 mm), and exhibited the expected IR and ^1H and ^{31}P NMR signals.[28]

Preparation of Acetoin and Acetoin Acetate. Commercial grade acetoin (Eastman no. P3788) was fractionally distilled at atmospheric pressure. Acetoin was obtained as a colorless liquid (bp 144–145 °C). It was mailed immediately from Stony Brook, N.Y., and was utilized promptly on arrival at Naperville, Ill.

Acetoin (15.0 g, 0.17 mol) was dissolved in 40 mL of dry pyridine; the solution was cooled to 0 °C, and acetic anhydride (40 mL) was added. The solution was stirred at 0 °C for 1 h and then left at 20 °C for 16 h. The mixture was then poured into ice-cold 10% sulfuric acid and extracted with ether (4 × 75 mL). The combined ether extracts were shaken with cold, saturated sodium carbonate solution (4 × 35 mL) and washed with water (1 × 35 mL). The ether layer was dried over sodium sulfate, filtered, and evaporated (30 mm at 20 °C). The crude acetoin acetate (17.18 g) was distilled under reduced pressure (46 mm), yielding (1) forerun bp <75 °C; (2) a bp 76–79 °C fraction; (3) a bp 79–81 °C fraction. Fractions 2 and 3 were redistilled and, from each, a middle fraction (bp 80–82 °C, 50 mm) was obtained. The two samples were shown to have identical purity by GC analysis (98–99%), and they were combined for further use (yield 6.70 g of pure acetoin acetate).

Mass Spectrometry. EI and FI mass spectra were measured on a CEC Model 21-110B instrument, with sample introduction via probe in most cases. A few EI spectra, as noted, were measured on other instruments, with sample introduction via batch inlet. Following

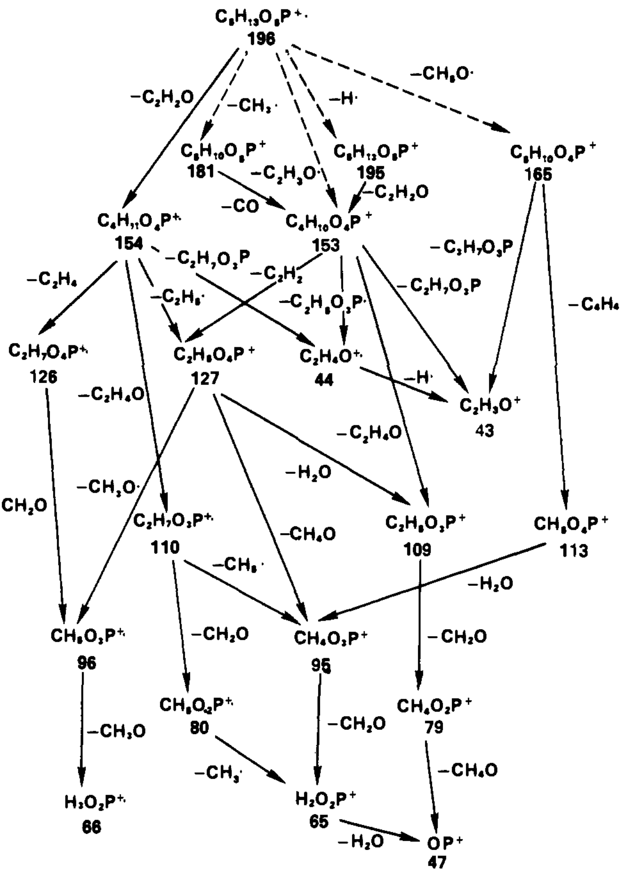


Figure 1. Decomposition of dimethylphosphoacetoin under electron impact.

transmittal by mail between our laboratories, samples were kept sealed under a nitrogen atmosphere in a refrigerator or freezer. The period before mass-spectral examination varied from a few hours to a few days; further measurements were made up to a few weeks after receipt, with the samples returned to storage in the refrigerator during the intervening time. Samples were then discarded, and fresh materials were prepared for further work. As an added precaution to minimize exposure to atmospheric oxygen and water, each sample was transferred from the glass storage vial to the probe tube under a blanket of nitrogen; the probe was then quickly injected into the ion source and the system was pumped down. In earlier measurements, the probe was heated indirectly by thermal contact with the ion source. Subsequently, a new probe,[29] equipped with its own heating coil and thermocouple and thermally insulated from the source, was put into service; it allowed us to fix the source temperature at about 250 °C and program the probe temperature directly rather than program the source temperature. The shift from indirect to direct heating evidently enabled the sample temperature to follow the measured temperature somewhat more closely, but the difference between them is uncertain and it may be considerable even with direct heating.[15] EI spectra were measured with 70-eV electrons; our FI operation has been described.[5] In both modes, a series of spectra was recorded as the temperature was gradually raised. FI spectra were recorded in analogue form; EI spectra, some analogue and some digital, the latter via the AEI DS50 system at a resolution of 10 000 (10%-valley definition), sufficient to allow unequivocal identification of elemental compositions. Analogue spectra were measured at lower resolution, ~2000, and at consequently higher sensitivity.

The EI analogue spectra showed numerous metastable peaks, which were of considerable interest as a means of defining decomposition paths.[24,26b] The apparent masses of many of these peaks, however, could be accounted for by two or more conceivable processes. In view of this ambiguity, we viewed these data as no more than preliminary, to be confirmed and supplemented by a metastable-scanning technique that allows unambiguous assignment: focusing on a selected fragment ion, decoupling the electric-sector voltage from the ion-accelerating voltage, and scanning the latter to increasing values.[23,24] All the deduced reaction paths reported here are based on measurements by the latter technique.

Table II. Selected Peaks from Metastable Scans on Dimethylphosphoacetoin

peak no.	mass scanned	precursor mass found	peak intensity, arbitrary units
1	127	196	7
2	127	154[a]	2030
3	127	153[a]	
4	109	153	3050
5	109	127	1100

[a] Unresolved.

An unexpected problem developed early in this work in that a number of peaks that were prominent in analogue EI spectra were missing in the corresponding digitally recorded spectra. In every such case, we found that the probable sample-derived ion and an ion that originated from the perfluorokerosene (PFK) introduced to calibrate the mass scale had masses so nearly equal that they were not resolved; the DS50 consequently assigned the peaks to PFK and deleted them from the normal output listing. Table I[30] shows the ions in question.

To supplement the published spectra of acetoin,[31] we prepared the compound and measured its EI and FI mass spectra on the 21-110B instrument, in this case with sample introduction via the batch inlet system. Our EI data are in qualitative accord with published spectra. However, both the FI spectrum and changes in the EI spectrum effected by momentarily opening the valve from the batch inlet, thus preferentially removing more volatile components, gave clear evidence for impurities, which appear to have contributed also to at least two of the three published spectra.[31b,c] The impurities, biacetyl and probably a trace of an aldol condensation/dehydration product, appear to introduce no ambiguity in terms of our concerns.

Some of the present metastable-scanning results directed our attention to the possible participation of parallel one- and two-step reaction paths from a common precursor to a common product. That a metastable peak may stem from a reaction path that includes more than a single step is well established.[24] However, when we have in the past encountered such an instance, say, for the sequence $A^+ \rightarrow B^+ \rightarrow C^+$, the intensity of the metastable peak corresponding to the overall reaction $A^+ \rightarrow C^+$ has usually been much lower than that for $B^+ \rightarrow C^+$.[24,32] In such measurements on DMPA, listed in Table II, the relative intensities of metastable peaks **1**, **2**, and **3** conform to this pattern and thus clearly indicate the parallel two-step paths:

$$\begin{tikzcd}[column sep=small, row sep=small] & 154^+ \arrow[dr] & \\ 196^+ \arrow[ur] \arrow[dr] & & 127^+ \\ & 153^+ \arrow[ur] & \end{tikzcd}$$

But intensities of peaks **4** and **5** do not so conform. We have taken such a reversal of relative intensities to indicate that a substantial part of the ion yield of mass 109 forms directly from precursor of mass 153, in competition with a two-step path through intermediate of mass 127.

Results

Dimethylphosphoacetoin. DMPA volatilized at low temperature (at probe temperature of ~50 °C when introduced via directly heated probe or at source temperature of ~100 °C with indirectly heated probe) and gave clean spectra with little indication of interference from thermal reactions. Table III[30] shows the EI spectrum so measured and, for comparison, a spectrum measured on a CEC Model 21-103 mass spectrometer, also using 70-eV electrons, but scanned electrically rather than magnetically, and with sample introduction via a batch inlet system at 250 °C; respective source temperatures for the two spectra were 245 and 250 °C. The spectra are in remarkably good accord despite differences in instrument geometry, scanning mode, and particularly method of sample introduction. The ion formulas listed are derived from high-resolution precise-mass measurements. Table IV[30] shows a typical FI spectrum, with sample introduction via indirectly heated probe, and initial source temperature of 100 °C. Figure 1 shows a

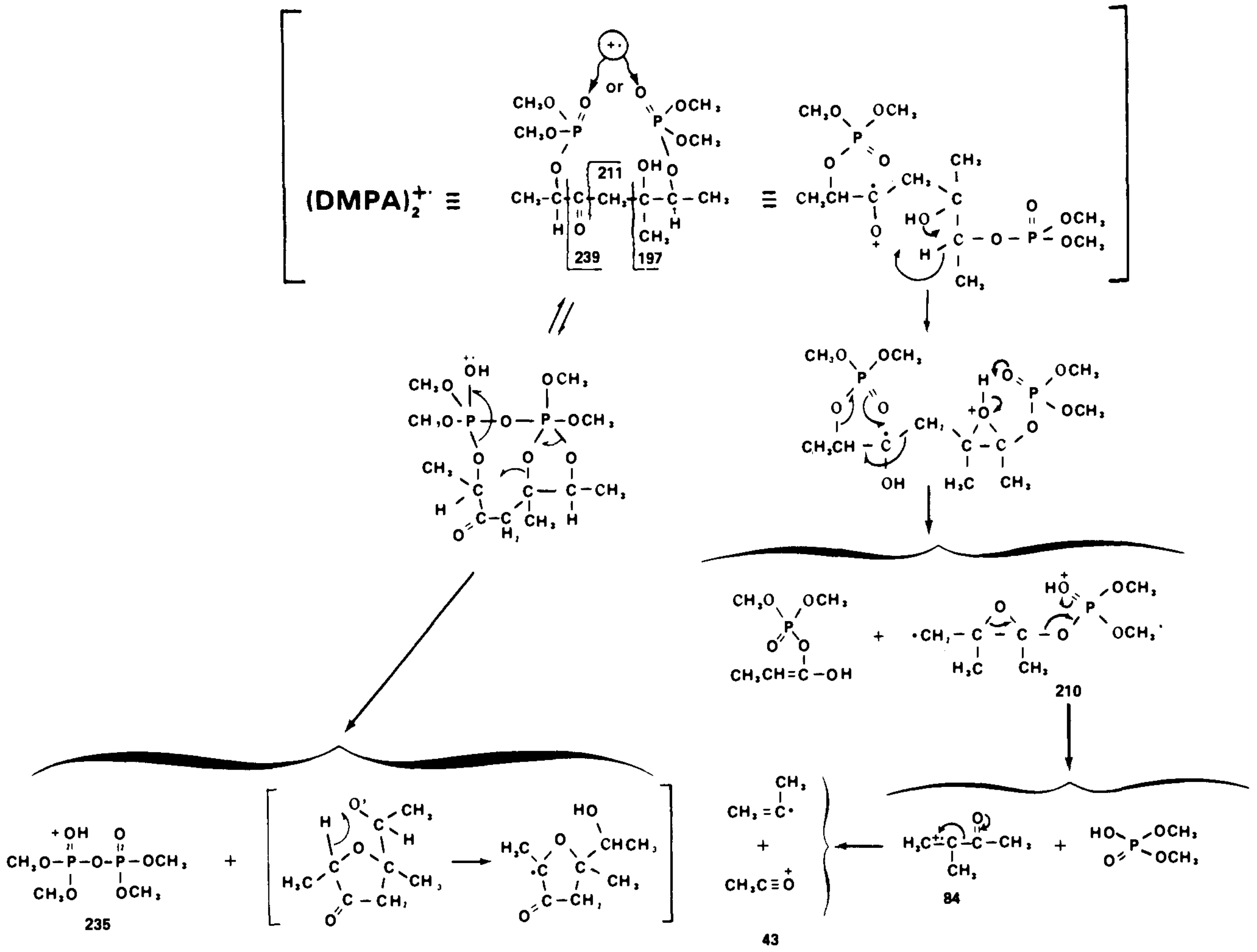
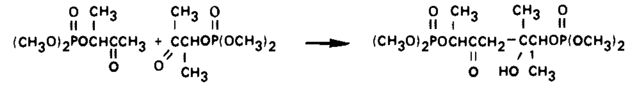


Figure 2. Some suggested ion origins by fragmentation of DMPA dimer molecular ion.

proposed decomposition scheme, based chiefly on the metastable-scanning results, with ion formulas derived from high-resolution precise-mass measurements. Both here and in subsequent decomposition schemes, reaction steps denoted by solid arrows are supported by metastable peaks; broken arrows identify steps deemed probable but not so supported. Part of the $C_2H_3O^+$ yield may form directly from the molecular ion as the product complementary to $C_4H_{10}O_4P^+$. A metastable scan on the peak at mass 43 indicates a precursor of mass 196, but the low intensity of the pertinent metastable peak suggests that it may arise via one or more of the multistep paths shown. Precursors of $C_2H_3O^+$ so identified include also $C_4H_6O^{+\cdot}$ and $C_4H_7O^+$, masses 70 and 71, which are doubtlessly derived from the 3-oxo-2-butyl group of the original molecule; we have omitted these ions from the figure as trivial.

The dominant primary processes in decomposition of ionized DMPA are (1) loss of acetyl radical to give $C_4H_{10}O_4P^+$, mass 153; (2) loss of ketene, implying a prior or possibly concerted hydrogen migration, to give $C_4H_{11}O_4P^{+\cdot}$, mass 154. The $C_4H_{10}O_4P^+$ ion breaks down further largely by loss of acetylene to give $C_2H_8O_4P^+$, mass 127, and of acetaldehyde to give $C_2H_6O_3P^+$, mass 109; superimposed on this segment of the network is the loss of water from $C_2H_8O_4P^+$ to give $C_2H_6O_3P^+$. The $C_4H_{11}O_4P^{+\cdot}$ ion breaks down further largely by loss of the elements of ethylene to give $C_2H_7O_4P^{+\cdot}$, of mass 126; of vinyl radical to contribute to the yield of $C_2H_8O_4P^+$, mass 127; and of acetaldehyde to give $C_2H_7O_3P^{+\cdot}$, mass 110. Losses of formaldehyde and, to a lesser extent, of methanol and methyl and methoxy radicals, prominent in further fragmentations, are presumably centered in the original methoxy groups.

In all our EI spectra of DMPA, the intensity at m/z 197 is substantially greater than that expected for the molecular ion containing ^{13}C in natural abundance, 6.9% of the intensity at 196. Precise-mass measurement confirmed the identity of this ion as $C_6H_{14}O_5P^+$, the protonated molecule, and a metastable scan identified its precursor as an ion of mass 239. Some of our spectra show a peak at m/z 239, and some show additional ones at m/z 210, 211, and 235, as listed in Table V,[30] all of low and variable intensity. Moreover, metastable scans on the peaks at masses 43 and 44 identify precursors of masses 84 and 85, respectively, for which precise-mass measurements pinpoint the compositions as $C_5H_8O^{+\cdot}$ and $C_5H_9O^+$. Both the carbon content of these ions and their highly variable relative intensities in replicate runs suggest that they derive from some component other than DMPA, and this suggestion was confirmed by metastable scanning, which identified masses of their precursors as 210 and 211, respectively. All of these peaks require the presence of molecular species heavier than DMPA, and they are plausibly accounted for by a dimer, $(DMPA)_2$, the result of a typical aldol condensation:



$$(CH_3O)_2P(O)OCH(CH_3)C(O)CH_3 + CH_3C(O)CH(CH_3)OP(O)(OCH_3)_2 \longrightarrow (CH_3O)_2P(O)OCH(CH_3)C(O)CH_2\text{–}C(OH)(CH_3)CH(CH_3)OP(O)(OCH_3)_2$$

The initial aldol product is assumed to be in equilibrium with the bis(pentaoxyphosphorane) shown in Figure 2.[33] Also shown in the figure are suggested ionic decomposition pathways to rationalize, at least in part, the observed fragment ions. Thus, the ion of mass 235 is probably protonated tetramethyl pyrophosphate and can be derived as shown. The suggested decomposition process, followed by a 1,5-hydrogen migration in

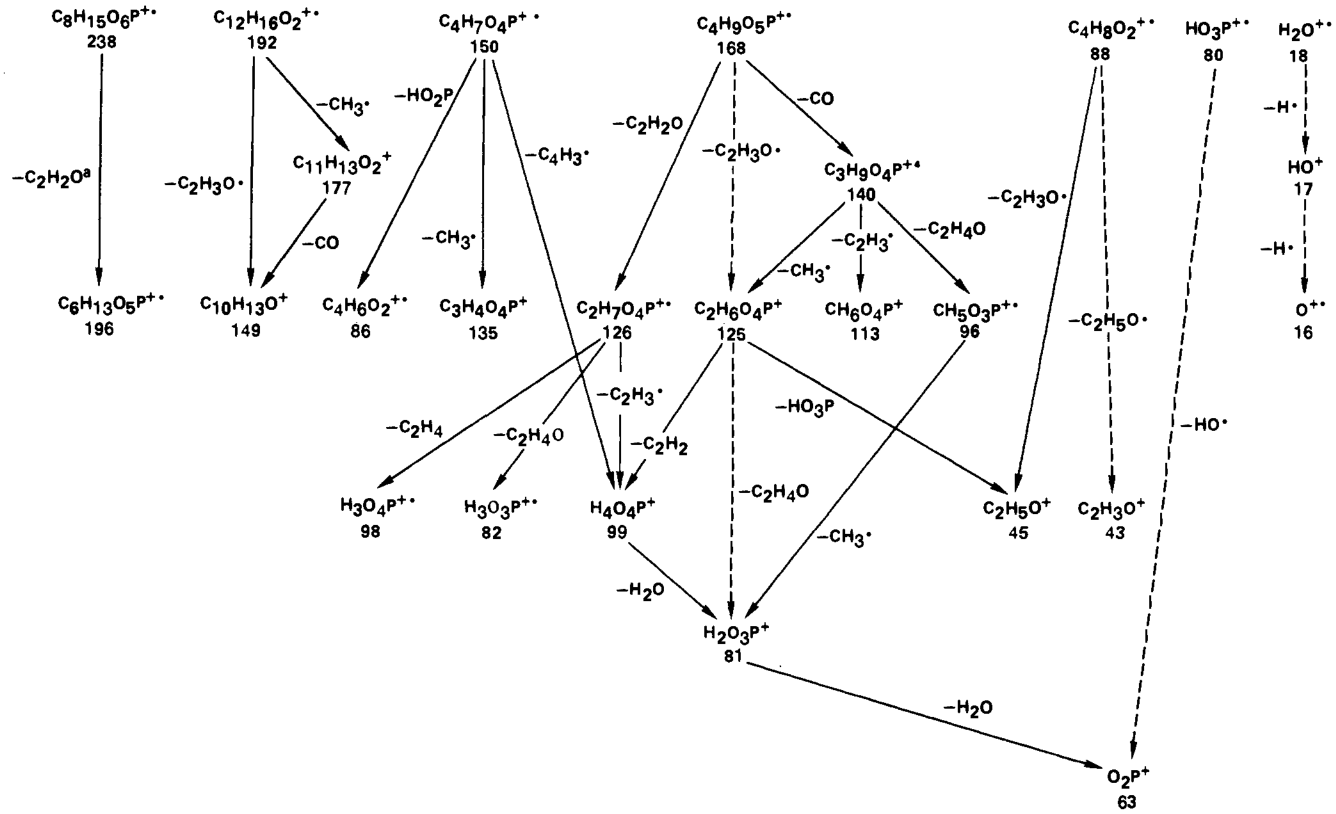


Figure 3. Decomposition of phosphoacetoin and associated thermal reaction products under electron impact. [a] The metastable peak corresponding to this reaction step was barely detectable above noise level and hence must be regarded as uncertain.

the neutral product, $C_8H_{13}O_3\cdot$, would yield the stable tertiary tetrahydrofuranonyl radical shown. Hydrogen migration coupled with bond rupture in the mass-211 ion pathway, as shown, would generate the ion of mass 210 and a neutral product that can be pictured as the enol of dimethyl propionyl phosphate. The epoxide structure shown for the radical cation of mass 210 seems able to account for its observed decomposition.

An EI spectrum of DMPA measured after 15 months storage under refrigeration (directly heated probe at 28 °C, source at 242 °C) shows a forest of small peaks at *m/z* values greater than 196. One peak stands out prominently, that for $C_{10}H_{19}O_6P^{+\cdot}$ at *m/z* 266, with an intensity slightly greater than that of the DMPA molecular ion at *m/z* 196. The composition $C_{10}H_{19}O_6P$ can be accounted for by aldol condensation/dehydration of DMPA with acetoin.

Phosphoacetoin. The spectra obtained from PAH_2 contain far greater contributions from thermal reactions than do those from DMPA. In runs utilizing a directly heated probe, PAH_2 peaks first attained substantial intensities in scans at initial probe temperatures of ~115 °C; with indirect heating, at initial source temperature close to 200 °C. At source temperatures much above 300 °C (indirect heating), even the FI spectra became so complex that they were useless. Even our cleanest EI and FI spectra, shown in Tables VI[30] and VII,[30] respectively, contain numerous peaks that must be attributed to thermal reaction products.

At the lowest temperatures at which PAH_2 was detected, both EI and FI spectra contained intense peaks for species of molecular weights 88, 150, and 192. With increasing temperature, these peaks and a weaker one at *m/z* 80, assigned unequivocally to $HO_3P^{+\cdot}$ on the basis of precise-mass measurement, increased sharply relative to those attributed to PAH_2, and, in FI spectra, the protonated-molecule peaks at *m/z* 89, 151, and 193—in addition to the expected PAH_2 peaks at *m/z* 169 (protonated monomer) and 337 (protonated dimer or disolvated proton)—were joined by others at *m/z* 221, 239, 245, 301, 319, 407, and 487. Probable molecular weights of the minimal additional components so indicated are 220, 238, and 244. The peaks at *m/z* 301, 319, 407, and 487, in the absence of clear correlation between FI and EI data, may be accounted for either by proton attachment to higher molecular weight components or by proton solvation by two or three of the various lighter molecules present.

Figure 3 shows a proposed decomposition scheme, based chiefly on metastable-scanning results and including thermal reaction products apparently contributing to the spectra in Tables VI and VII. The probable structures and origins of these thermal reaction products are listed in Table VIII; additional products, observed in spectra measured at higher temperatures, are listed in Table IX.

The dominant primary processes in the decomposition of ionized PAH_2 parallel those of DMPA: (1) loss of acetyl radical to give $C_2H_6O_4P^+$, mass 125; (2) hydrogen migration and loss of ketene to give $C_2H_7O_4P^{+\cdot}$, mass 126. Continuing the parallel behavior, $C_2H_6O_4P^+$ breaks down further by loss of acetylene to give $H_4O_4P^+$, mass 99, and of acetaldehyde to give $H_2O_3P^+$, mass 81, and $H_4O_4P^+$ undergoes dehydration to contribute further to the yield of $H_2O_3P^+$. Similarly, $C_2H_7O_4P^{+\cdot}$ breaks down by loss of vinyl radical to contribute to the yield of $H_4O_4P^+$, mass 99, of acetaldehyde to give $H_3O_3P^{+\cdot}$, mass 82, and of C_2H_4 to give $H_3O_4P^{+\cdot}$, mass 98, the phosphoric acid radical cation.

A third primary process, loss of CO to give $C_3H_9O_4P^{+\cdot}$, mass 140, implies prior migration of a methyl radical. Such loss of CO from a nonterminal position in molecular ions has been reported as a minor pathway in the mass spectra of a variety of carbonyl compounds containing at least one additional site of unsaturation.[34] In view of the observed further decomposition of $C_3H_9O_4P^{+\cdot}$, in which the neutral particles lost contain either one or two carbons, the phosphoryl doubly bonded oxygen atom seems the most likely site of the translo-

Table VIII. Probable Thermal Reaction Products Contributing to Mass Spectra of Phosphoacetoin

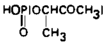
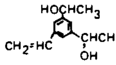
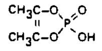
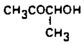
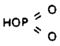
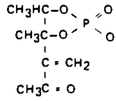
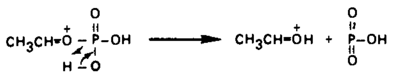
Elemental composition	Nominal molecular weight	Suggested structure	Suggested origin	M/z at which the product contributes
$C_8H_{15}O_6P$	238	 $HOP(=O)(OCH(CH_3)COCH_3)_2$	Esterification of PAH_2 with acetoin	EI: 196 FI: 239
$C_{12}H_{16}O_2$	192		Trimerization of acetoin with loss of 4 H_2O	EI: 192, 177, 149 FI: 194, 193, 192, 175
$C_4H_7O_4P$	150		Loss of H_2O from PAH_2	EI: 150, 135, 99, 86 FI: 151, 150
$C_4H_8O_2$	88	 $CH_3COCH(CH_3)OH$	$PAH_2 \rightarrow C_4H_8O_2 + HO_3P$	EI: 88, 45, 43 FI: 89, 88
HO_3P	80	 $HOP(=O)=O$		EI: 80, 63 FI: None
H_2O	18	HOH	See reactions listed above for $C_{12}H_{16}O_2$ and $C_4H_7O_4P$	EI: 18, 17, 16 FI: Not scanned

Table IX. Supplemental List of Probable Thermal Reaction Products Contributing to Mass Spectra of Phosphoacetoin

Probable elemental composition	Nominal molecular weight	Suggested structure	Suggested origin	M/z at which the product contributes
$C_8H_{18}O_{10}P_2$	336		Dimerization of PAH_2	FI: 337
$C_8H_{16}O_9P_2$	318		Condensation of PAH_2 with $C_4H_7O_4P$	FI: 319
$C_8H_{14}O_8P_2$	300		Dimerization of $C_4H_7O_4P$	FI: 301
$C_{16}H_{20}O_2$	244		Condensation of 4 acetoin molecules with loss of 6 H_2O	FI: 245
$C_8H_{13}O_5P$	220		Aldol condensation of PAH_2 with acetoin, esterification, and dehydration	EI: 220, 150, 149; probably also 151 FI: 221

cated methyl group.

Of particular interest with reference to the mechanistic questions centering around monomeric metaphosphate species[5] is the decomposition of $C_2H_6O_4P^+$ to metaphosphoric acid and $C_2H_5O^+$, mass 45, presumably by the reaction



$$CH_3CH{=}\overset{+}{O}-\overset{O}{\overset{\|}{P}}-OH \longrightarrow CH_3CH{=}\overset{+}{O}H + \overset{O}{\overset{\|}{P}}-OH$$

Assignment of the $C_4H_8O_2^{+\cdot}$ and $HO_3P^{+\cdot}$ peaks to the molecular ions of thermally produced acetoin and metaphosphoric acid is supported by our failure to find any metastable peaks denoting ionic precursors for them. Identification of acetoin by comparison of the mixture spectra with our own and literature[31] reference spectra is further supported by identical results of metastable scanning of the prominent peaks at *m/z* 43 and 45 ($C_2H_3O^+$ and $C_2H_5O^+$) in spectra obtained with PAH_2, and MPAH as well, and authentic acetoin. In all three cases, we observed an intense metastable peak for the process

$$88^+ \rightarrow 45^+ + 43;\ \text{i.e.,}\ C_4H_8O_2^{+\cdot} \rightarrow C_2H_5O^+ + \cdot C_2H_3O \qquad (1)$$

but none for the complementary process

$$88^+ \rightarrow 43^+ + 45;\ \text{i.e.,}\ C_4H_8O_2^{+\cdot} \rightarrow C_2H_3O^+ + \cdot C_2H_5O \qquad (2)$$

The data imply that process 2 is essentially complete by the time the ions involved exit from the ionization chamber, about 1 μs after the ionizing event, but that process 1 is still occurring at a high enough rate to permit ready detection while the ions are in the first field-free region, some 2 or more μs after ionization.[26c] The reason for the difference is not obvious to us.

The inference that monomeric metaphosphoric acid is present in the gas phase in the ionization chamber appears probable despite our failure to detect it in FI spectra. Under our experimental conditions, the FI spectra are dominated by protonated molecules, especially of acidic components, rather than molecular radical cations. Such formation of protonated molecules is believed to be a surface reaction.[22,35] That is, it requires prior adsorption on the anode, and falls in the category of processes that are best viewed as field-desorption components of nominally FI spectra.[5] If HPO_3 undergoes desorption at all, it may occur only after conversion to some other, unidentified, species.

The presence of acetoin in the system apparently leads to, and, conversely, is further evidenced by, several additional molecular species: $C_{12}H_{16}O_2$, of molecular weight 192; $C_{16}H_{20}O_2$, 244; $C_8H_{15}O_6P$, 238; $C_8H_{13}O_5P$, 220. Our suggestion in Table VIII of the structure bis(1-hydroxyethyl)styrene for $C_{12}H_{16}O_2$ is based on its decomposition paths, shown in Figure 3. 1-Phenylethanol,[36] 1-*p*-tolylethanol,[37] and, if replacing the terminal methyl group with a hydrogen atom is not deemed to invalidate the analogy, benzyl alcohol[38] break down similarly under EI. Aldol cyclotrimerization/dehydration of acetoin would lead to tris(1-hydroxyethyl)benzene, and loss of a further molecule of water from one hydroxyethyl group would yield the structure shown and account for the observed mass-spectral features. The structure and manner of formation of $C_{16}H_{20}O_2$ are obscure, but the composition is equivalent to four molecules of acetoin minus $6H_2O$. Hence, we presume that it arose also from acetoin by some sort of condensation/dehydration process. The composition of $C_8H_{15}O_6P$ is equivalent to PAH_2 + acetoin − H_2O; in view of its observed decomposition by loss of ketene, we formulate its structure, by analogy with PAH_2 and DMPA, as diacetoin phosphate, arising by esterification of PAH_2 with acetoin. The product of formula $C_8H_{13}O_5P$ differs in composition from $C_8H_{15}O_6P$ simply by the elements of H_2O. But, unlike the acetoin phosphate esters, we find no evidence that the former loses $CH_3CO\cdot$ or CH_2CO under EI; we infer that it does not contain an acetoin ester grouping. Instead, it breaks down variously by primary loss of $C_4H_5O\cdot$, C_4H_6O, and $C_4H_7O\cdot$. Figure 4 shows the proposed formation via a condensation-esterification-dehydration sequence and decomposition under EI of a structure suggested in Table IX to account for the data.

A further product of particular interest, because it appears to form via a monomeric metaphospahte intermediate, is the probable thermal dehydration product, $C_4H_7O_4P$, molecular weight 150. Some measure of uncertainty is associated with this assignment because the pertinent metastable scan showed a weak peak denoting an ionic precursor of mass 220, as indicated in Table IX:

$$C_8H_{13}O_5P^{+\cdot} \rightarrow C_4H_7O_4P^{+\cdot} + C_4H_6O$$

But we believe that this latter path is only a minor contributor to the observed intensity at *m/z* 150. Water might be eliminated either between a phosphoryl hydroxyl and the hydroxyl of the enol form of PAH_2 or between the two phosphoryl hydroxyl groups. If the first of these reactions occurred, however, one would expect MPAH to undergo the analogous reaction to yield the methyl derivative, $C_5H_9O_4P$, molecular weight 164. We were unable to find any evidence for such a product in our MPAH spectra; hence the second pathway seems more probable. We therefore view the structure initially formed as acetoin metaphosphate. But the high electrophilicity of monomeric metaphosphate[39-43] would be expected to bring

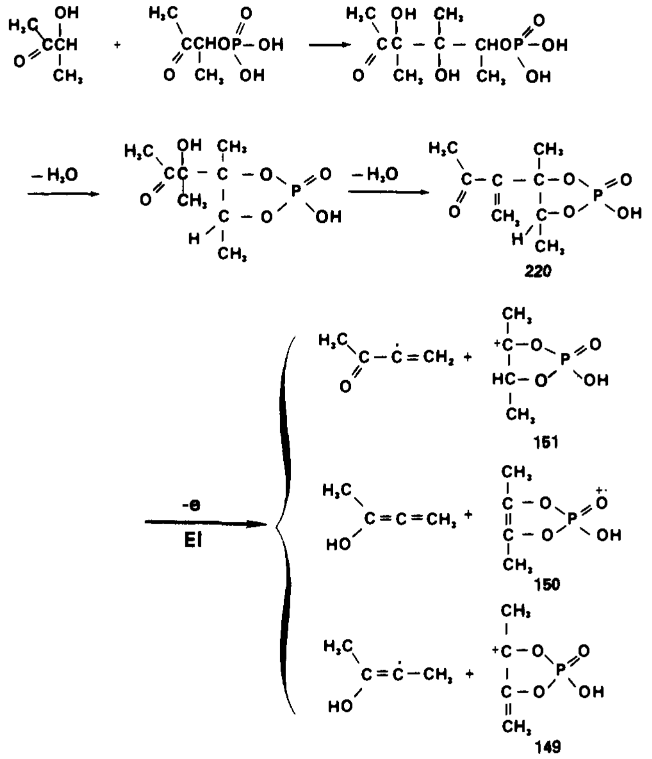
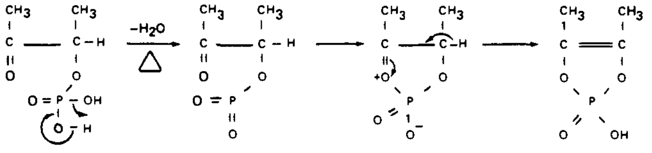


Figure 4. Proposed formation and EI-induced decomposition of $C_8H_{13}O_5P$, molecular weight 220.

about rapid reorganization to form the cyclic enediol phosphate:



A sample of this cyclic phosphate was synthesized at Stony Brook, N.Y., and its mass spectrum was measured promptly upon arrival at Naperville, Ill., but it was found to have already suffered extensive thermal degradation. In fact, we were unable to detect any of the original compound. However, a conventional EI spectrum of the derived methyl ester,[44] measured several years ago,[36] shows normal peaks at the masses to be expected if the methyl derivative underwent the same three primary decomposition reactions that we find for the present component, and metastable peaks that parallel two of the three reactions: loss of $\cdot CH_3$, mass 15, and loss of $\cdot C_4H_3$, mass 51. The loss of CH_3PO_2, paralleling the presently observed loss of HPO_2, to produce $C_4H_6O_2^{+\cdot}$, mass 86, might also have been confirmed by metastable scanning, but we were not equipped to make such scans at the time that work was done. Thus, the available data appear consistent with the view that $C_4H_7O_4P$ forms initially as acetoin metaphosphate, which then converts to the cyclic enediol phosphate pictured above.

The three heavier species listed in Table IX are essentially dimers. The formula of $C_8H_{18}O_{10}P_2$, molecular weight 336, corresponds to a dimer of PAH_2; that of $C_8H_{16}O_9P_2$, 318, a condensation product of PAH_2 with $C_4H_7O_4P$; that of $C_8H_{14}O_8P_2$, 300, a dimer of $C_4H_7O_4P$. The data on hand are insufficient to support further speculation.

Several of the reactions postulated to account for other products from PAH_2 also give rise to water and presumably contribute to the H_2O peaks observed and listed in Table VIII.

Methylphosphoacetoin. MPAH exhibits the seemingly most complex behavior of the three phosphoacetoins. But the EI and FI spectra complement each other well and, taken together, they furnish a basis for reconstructing much of the underlying chemistry, both thermal and ionic, despite the complexity. As the sample temperature is raised, lower boiling components diminish and are replaced by higher boiling ones; the latter increasingly undergo thermal degradation to lighter products, some of which appear identical with original components that had volatilized earlier.

At source temperatures from about 60 to 100 °C (sample probe heated indirectly), the spectra are dominated by DMPA, which must have formed in the period between the synthesis and the mass-spectral examination, despite refrigeration and protection from light and air. MPAH first appears at about 100 °C, and at 160 ° it becomes dominant as the DMPA content drops rapidly. The MPAH dimer molecular ion, mass 364, first appears at about the same temperature as the monomer molecular ion. In EI spectra, the dimer:monomer molecular-ion intensity ratio, $M_2^{+\cdot}$:$M^{+\cdot}$, where M ≡ a molecule of MPAH, quickly attains a maximum value of 0.02—0.10, and then diminishes as the temperature increases and peaks attributed to PAH_2, PAH_2 less H_2O, and acetoin build up. In FI spectra, as shown in Table X,[30] the M_2H^+:MH^+ intensity ratio—that is, of the protonated dimer or disolvated proton to the protonated monomer—increases to a value of nearly 3 at ~200-230 °C; then it drops to values of ~0.4-0.6 with further temperature increase to ~320 °C. These highest temperatures are accompanied by intensity increases also, relative to that of MH^+, of peaks at masses 89, 151, 169, 193, 197, 221, 245, 351, and 533. These masses correspond to a series of protonated molecules: acetoin, PAH_2 less H_2O, PAH_2, an acetoin-derived aldol condensation/dehydration product, DMPA, the aldol product $C_8H_{13}O_5P$ (cf. Table IX), another acetoin-derived condensation/dehydration product, MPAH + PAH_2, and 2MPAH + PAH_2, respectively. Peaks at *m/z* 561 and 575, corresponding to $(DMPA)(MPAH)_2H^+$ and $(DMPA)_2(MPAH)H^+$, appear briefly in two scans in which both DMPA and MPAH are present at high levels, then vanish except for a trace at *m/z* 561 that appears in the final scan, accompanying $(DMPA)H^+$ at *m/z* 197. These trends suggest that MPAH dimer volatilizes somewhat less readily than the monomer, and hence attains maximum concentration in the vapor at a higher temperature, and that further increase of temperature causes progressively more extensive decomposition of the dimer to monomer and the other products listed.

The EI spectrum A in Table XI[30] was measured at an initial probe temperature (directly heated) of 30 °C, where DMPA in the vapor phase is rapidly being replaced by MPAH. Spectrum B is perhaps the closest approach we have attained to a spectrum of "pure" MPAH. Figure 5 shows a decomposition scheme assembled from metastable scans made under conditions that yield a mixture of mainly DMPA, MPAH, and PAH_2. The reaction networks found, and shown here, for $C_6H_{13}O_5P^{+\cdot}$ and $C_4H_9O_5P^{+\cdot}$ confirm beyond a doubt the identities of these species as the molecular ions of DMPA and PAH_2.

The dominant primary processes in decomposition of ionized MPAH parallel those of DMPA and PAH_2: (1) loss of acetyl radical to give $C_3H_8O_4P^+$, mass 139; (2) hydrogen migration and loss of ketene to give $C_3H_9O_4P^{+\cdot}$, mass 140. Again continuing the parallel, $C_3H_8O_4P^+$ breaks down further by loss of acetylene to give $CH_6O_4P^+$, mass 113, and of acetaldehyde to give $CH_4O_3P^+$, mass 95; $CH_6O_4P^+$ undergoes dehydration to contribute to the yield of $CH_4O_3P^+$. Likewise, $C_3H_9O_4P^{+\cdot}$ breaks down further by loss of vinyl radical to contribute to the yield of $CH_6O_4P^+$, mass 113, of acetaldehyde to give $CH_5O_3P^{+\cdot}$, mass 96, and of C_2H_4 to give $CH_5O_4P^{+\cdot}$, mass 112. Also paralleling the behavior of PAH_2, $MPAH^{+\cdot}$ undergoes a third primary process, loss of CO, to give $C_4H_{11}O_4P^{+\cdot}$, mass 154, implying prior migration of the ini-

Table XIII. Temperature Dependence of *m/z* 365:364 and 183:182 Intensity Ratios in EI Spectra of MPAH[a]

initial source temp, °C	*m/z* 365:364 intensity ratio	initial source temp, °C	*m/z* 183:182 intensity ratio
118	0.12	108	0.14
162	0.22	125	0.41
220	0.17	150	0.61
280	1.52	178	0.78
		210	1.29

[a] Measured on CEC Model 21-110B instrument, with sample introduction via probe heated by thermal contact with source; electron energy, 70 eV. The data in columns 1 and 2 were obtained via analogue recording; those in columns 3 and 4, via DS50 output.

tially terminal methyl group. As in DMPA, loss of formaldehyde is prominent in further fragmentations.

Table XII[30] shows two EI scans, made at initial source temperatures (indirectly heated probe) of 118 and 280 °C, that focus mainly on MPAH dimer and thermal reaction products. Comparison of the two spectra shows a marked increase at the higher temperature of intensity at *m/z* 365 relative to that at *m/z* 364. This observation prompted us to examine the *m/z* 365:364 intensity ratio as a function of temperature, with the results shown in Table XIII; also listed there are the corresponding data for monomeric ions, (MPAH)H$^+$ and MPAH$^{+\cdot}$, *m/z* 183 and 182. The data in columns 1 and 2 are taken from the series of scans that yielded the spectra in Table XII. Because intensities at *m/z* 183 and 182 were off scale in the higher temperature scans of this series, the data displayed in columns 3 and 4 were taken from a DS50 run, measured at higher resolution and hence lower sensitivity. The numerical values of these intensity ratios varied widely from one run to another, but the direction of their temperature dependence, as measured from a series of sequential scans comprising a run, was consistent. At 118 °C, the *m/z* 365:364 intensity ratio can be accounted for simply in terms of naturally occurring heavy-isotopic species, but with increasing temperature it greatly exceeds this value. Even at 108 °C, the *m/z* 183:182 intensity ratio is greater by a factor of 2 than can be so accounted for, and it too increases rapidly with increasing temperature. Just as (DMPA)H$^+$ in the EI spectrum of DMPA was found to arise from decomposition of a heavier species, which in turn was seemingly derived from dimer, so also (MPAH)H$^+$, mass 183, was found to stem from MPAH dimer; the parallel temperature dependences evident in Table XIII suggest that (MPAH)$_2$H$^+$, mass 365, most likely stems from MPAH trimer and perhaps higher oligomers.

The scheme of Figure 6 shows the decomposition of the MPAH dimer molecular ion and the protonated dimer. Scans made on both ions of *m/z* 183 and 182 yielded asymmetric peaks that we assigned to unresolved pairs corresponding to precursors of *m/z* 365 and 364. The broken arrow leading from *m/z* 365 to 225 in the figure represents a suspected second component here also, unresolved from the metastable peak for the process $364^+ \rightarrow 225^+ + 139$. All other broken arrows in this figure denote processes for which no metastable scans were made.

The disproportionation $2\text{MPAH} \rightarrow \text{PAH}_2 + \text{DMPA}$ most likely takes place via a dimeric intermediate, and both this thermal process and the three primary ionic decomposition reactions shown in Figure 6 can be rationalized by the dimer formulation pictured in Figure 7. The mobility required to effect the disproportionation is not understandable in terms of four-coordinate phosphorus, but follows readily from the loss of integrity of phosphorus-oxygen bonds that characterizes five-coordinate phosphorus.[45] The central eight-membered ring in the configuration in which both phosphorus atoms have become five coordinate resembles the favored eight-membered ring occurring in P_4O_{10} and tetrametaphosphate.[46] Once the cage has been constructed, the phosphorus atoms are close together and the bis(hydroxymethoxyphosphorane) can convert to the dihydroxyphosphorane-dimethoxyphosphorane by a mechanism similar to that described for the molecular rearrangement of a cyclic sugar phosphate.[47] The essential step is the translocation of hydroxyl and methoxyl groups bonded to five-coordinate phosphorus. Molecular models disclose no steric hindrance to the formation of the postulated intermediates. An aldol product analogous to that proposed for the DMPA dimer as shown in Figure 2 may also form, but it would appear an unlikely source of either the disproportionation products or the ionic products arising by primary loss of acetyl radical and of ketene.

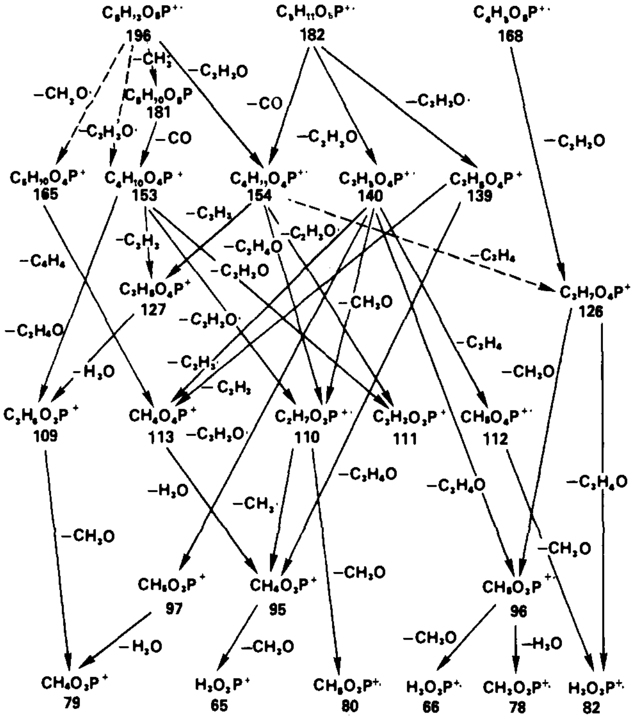


Figure 5. Decomposition of methylphosphoacetoin and associated thermal reaction products under electron impact at "moderate" temperature.

Acetoin Acetate. The EI spectrum was measured (1) on the 21-110B instrument with sample introduction via probe, the source temperature at 200 °C, and the probe temperature programmed from an initially subambient value; (2) on the 21-110B with sample introduction via batch inlet and source and inlet temperatures, respectively, of 205 and 155 °C; (3) on a Du Pont Model 21-104 instrument, using electrical scanning, with sample introduction via batch inlet and source and inlet temperatures, respectively, of 207 and 147 °C. The results obtained from the three procedures were nearly identical, with only the barest indication of impurity, a trace, seemingly, of aldol product derived from acetoin. A 21-110B batch-inlet run showed traces of acetic acid and C_4H_6O, presumably methyl vinyl ketone, which undoubtedly arose by incipient thermal decomposition of the acetate. A spectrum from a 21-110B probe-injection run is displayed in Table XIV,[30] and a proposed decomposition scheme in Figure 8. Intensities at *m/z* 88 and 44 are attributed largely to the naturally occurring heavy-isotopic species $^{13}C^{12}C_3H_7O_2^+$ and $^{13}C^{12}CH_3O^+$, respectively; however, correction for these contributions leaves small but real residues, as listed in the table, due to $C_4H_8O_2^{+\cdot}$ and $C_2H_4O^{+\cdot}$.

Each of the two defined primary processes, loss of $CH_3CO\cdot$ and of $CH_2{=}CO$ to yield $C_4H_7O_2^+$ and $C_4H_8O_2^{+\cdot}$, respec-

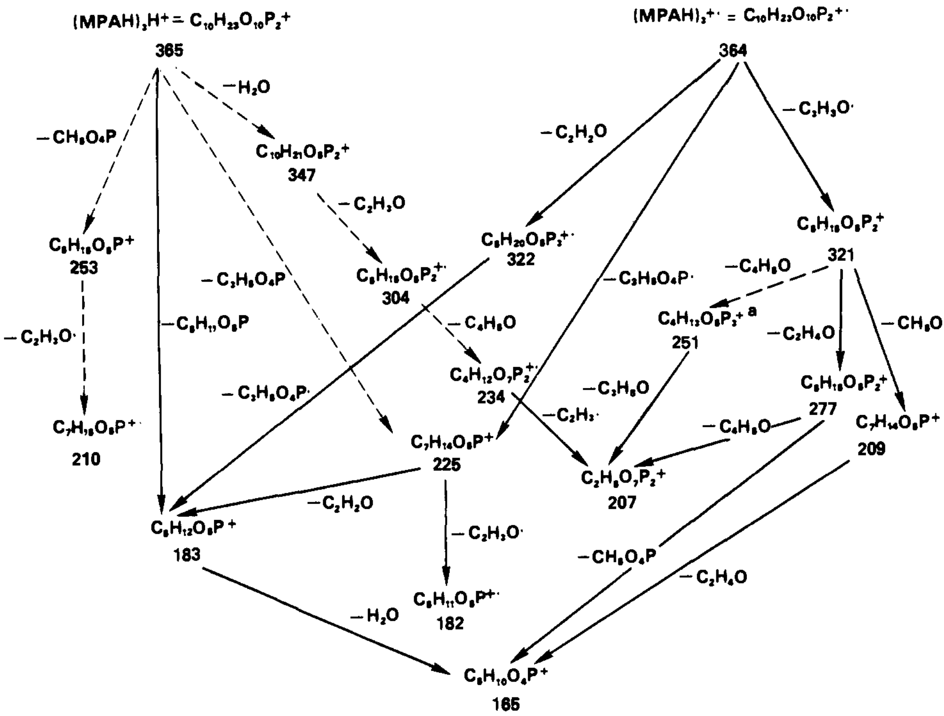


Figure 6. Decomposition of methylphosphoacetoin dimer under electron impact. [a] No normal peak was detected for this ion. The formula is suggested as probable.

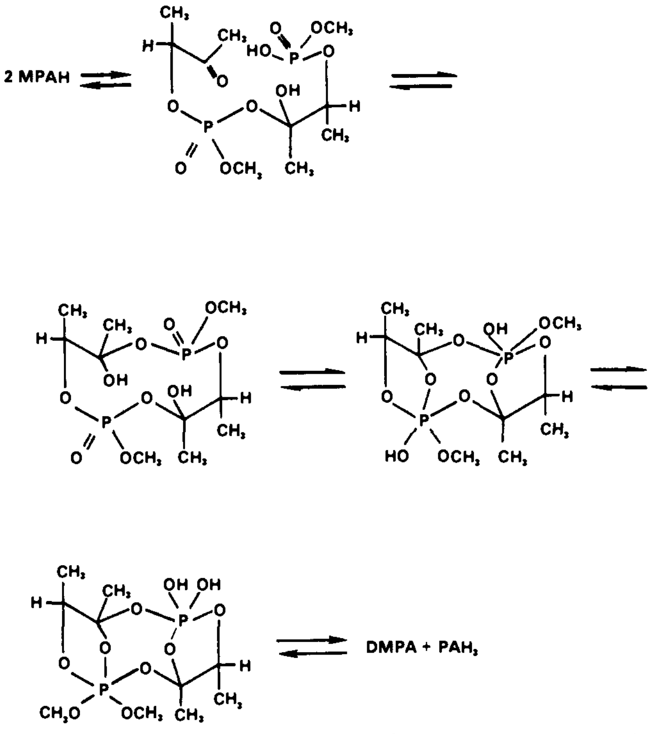


Figure 7. Suggested structure of the methylphosphoacetoin dimer, and mechanism for its disproportionation.

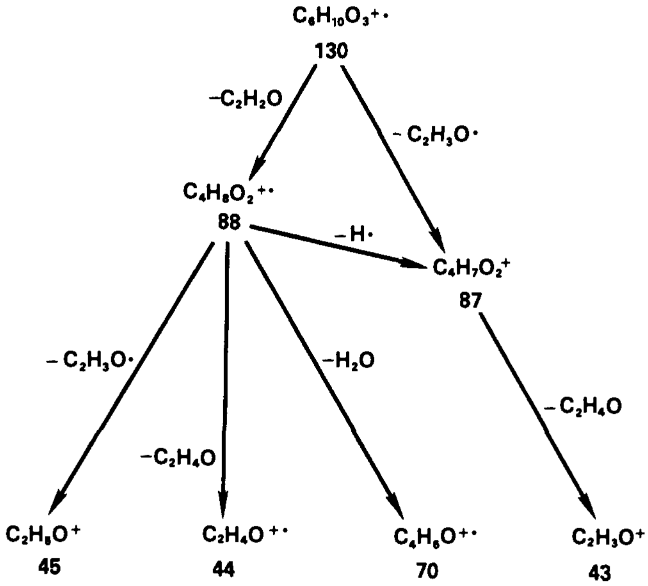


Figure 8. Decomposition of acetoin acetate under electron impact.

tively, could be centered in either the acetoin acetyl group or the acetate acetyl group. Secondary loss of $C_2H_3O\cdot$ from $C_4H_8O_2^{+\cdot}$ parallels the behavior of acetoin but is not observed following primary loss of ketene in the phosphoacetoins. Secondary loss of acetaldehyde did, however, follow the loss of ketene from all three of the phosphoacetoins. Therefore we conclude that both ends of the molecule probably contribute to the loss of ketene from acetoin acetate. Just as the intensity of the normal peak for $C_4H_8O_2^{+\cdot}$ is much lower than that for $C_4H_7O_2^+$, so also are the metastable-peak intensities for the processes

$$130^+ \rightarrow 88^+ + 42;\ \text{i.e., } C_6H_{10}O_3^{+\cdot} \rightarrow C_4H_8O_2^{+\cdot} + C_2H_2O$$

$$88^+ \rightarrow 87^+ + 1;\ \text{i.e., } C_4H_8O_2^{+\cdot} \rightarrow C_4H_7O_2^+ + C_2H_3O\cdot$$

much lower than that—specifically, 13 and 6% as great—for the process

$$130^+ \rightarrow 87^+ + 43;\ \text{i.e., } C_6H_{10}O_3^{+\cdot} \rightarrow C_4H_7O_2^+ + C_2H_3O\cdot$$

Thus, the dominant reaction sequence is clearly

$$C_6H_{10}O_3^{+\cdot} \xrightarrow{-C_2H_3O\cdot} C_4H_7O_2^+ \xrightarrow{-C_2H_4O} C_2H_3O^+$$

Primary loss of acetyl radical from either end of the molecule might reasonably be expected to trigger loss of acetaldehyde, and we assume that both processes contribute.

Discussion

At first glance, the behavior exhibited by each of the three phosphoacetoins looked markedly different from that of the other two. In retrospect, however, the similarities among them appear more pervasive than the differences, which proved most useful in this investigation by virtue of helping define questions and of furnishing points of departure. The differences have their genesis in the differing numbers of acidic groups on the phosphorus atom, in part via such trivial effects as differences in volatility. Our spectra reflect the combined effects of three superimposed layers of chemistry, two thermal and one EI induced.

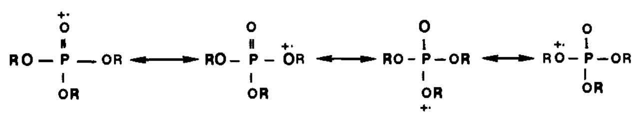
Thermal Reactions. The first thermal layer is condensation, including in particular dimerization, which may proceed either by phosphoryl attack on a carbonyl center or by an aldol reaction between the acetoin groups of the two participating ester molecules. The second thermal layer consists of decomposition, and some of the products so formed, in particular acetoin, may in turn condense with themselves, with the original ester, or with other products of condensation or decomposition. Reactions in both of these categories evidently proceed in the stored ester samples, despite our precautions, and are accelerated upon introduction to the ion source in consequence of the heating needed to effect volatilization. In part, these reactions may reflect the existence of equilibria in the liquid phase that had not been detected by IR or NMR spectrometry because of unfavorable equilibrium position or low rate of establishment. To recapitulate, we have called attention above to (1) the thermal disproportionation of MPAH into DMPA and PAH_2 in the absence of added catalysts; (2) the decomposition of MPAH and PAH_2, but not of DMPA, into acetoin and methyl metaphosphate or metaphosphoric acid, respectively; (3) dehydration of PAH_2 coupled with an intramolecular reorganization to yield apparently a transient acetoin metaphosphate, which transforms rapidly to a cyclic enediol phosphate. These various reactions compete with each other and with other processes. Even the neutral ester, DMPA, which for the most part gives clean, reasonably reproducible spectra with little call for any special precautions, appears to undergo aldol condensation, possibly assisted by intra- or intermolecular abstraction of the weakly acidic α hydrogen by the phosphoryl group:

$$>PO + CH_3CO- \rightleftharpoons >PO^+H + {}^-CH_2CO-$$

PAH_2 is the highest boiling of the three monomers, and its dimer is apparently the highest boiling of the dimers; at the temperatures needed to volatilize them, both the monomer and dimer undergo extensive thermal decomposition. MPAH dimer volatilizes at moderate temperatures, only slightly higher than that at which we first observe the monomer, and undergoes extensive thermal decomposition only at higher temperatures. Clearly, the low MPAH dimer:monomer molecular-ion intensity ratio even at temperatures at which it is maximized, like our failure to observe directly dimer molecular ions of DMPA and PAH_2, does not adequately reflect the extent of dimer contributions to the spectra. Quite apart from intervening thermal decomposition, all the dimer structures suggested have numerous weak bonds and one would expect the molecular-ion peaks in their EI mass spectra to be of low intensity.[48] Molecular-ion intensities even of the monomeric esters are no more than a few percent of those of the most intense peaks in the EI spectra.

The extent and complexity of the thermal chemistry that cluttered the scene in our attempts to measure the mass spectra of the three phosphoacetoins appear common to work with organic phosphates and related species in other contexts as well. Those products of Westheimer's pyrolysis/trapping experiments that were characterized and offered as evidence for the existence of monomeric methyl metaphosphate as an intermediate comprised only some 1-5% of the total products.[39] The bulk of the products was described as "polymeric material". A number of 1-(dialkylphosphoryl)imidazoles have been reported to undergo extensive thermal decomposition at surprisingly low temperatures.[49] A recent paper on field-desorption mass spectrometry, which was chosen as a more promising approach than EI, of dipalmitoylphosphatidylcholine reports erratic variation of the spectra obtained,[50] paralleling our experience in the work reported here. This variation included, in particular, increased spectral contributions at masses well in excess of that of the molecular ion as the anode temperature was increased.

Scheme II



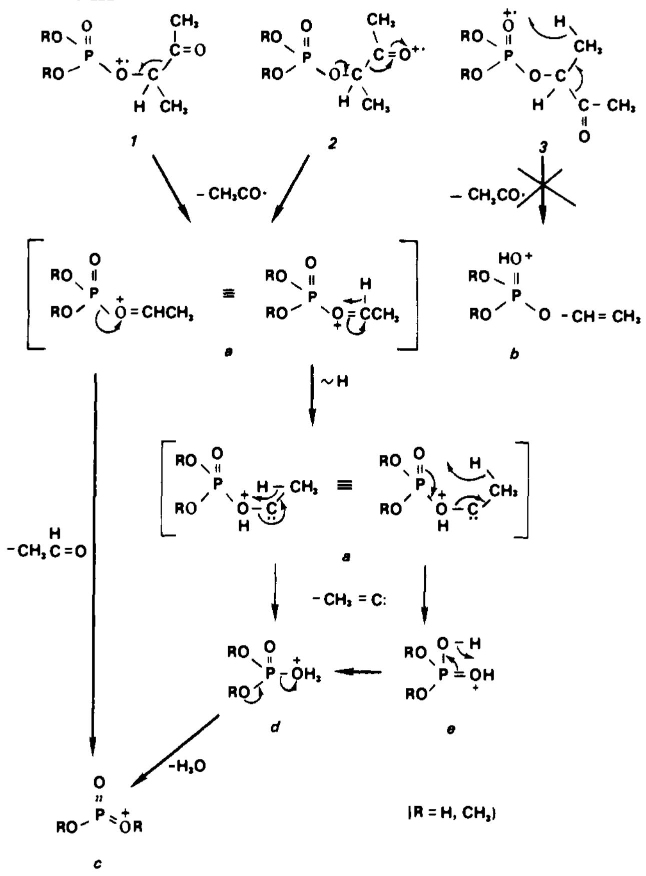
Each R = H or alkyl, for example

Reactions Induced by EI. In attempting to formulate mechanisms to rationalize our experimental data, we have followed the conventional practice—at least a useful mnemonic device—of picturing the charge as localized, usually in a nonbonding orbital.[51a,52] Specifically, in ions stemming from phosphate esters, the most plausible sites appear to be on the phosphoryl oxygen atoms.[51b] The resonance that may be represented formally by moving the charge and odd electron among the phosphoryl oxygens, as illustrated in Scheme II, can perhaps help to account for the large fraction of total ion current contributed by odd-electron species, i.e., radical cations, in the mass spectra of these phosphates. The spectrum of acetoin acetate, for example, contrasts markedly with those of the phosphoacetoins in this respect.

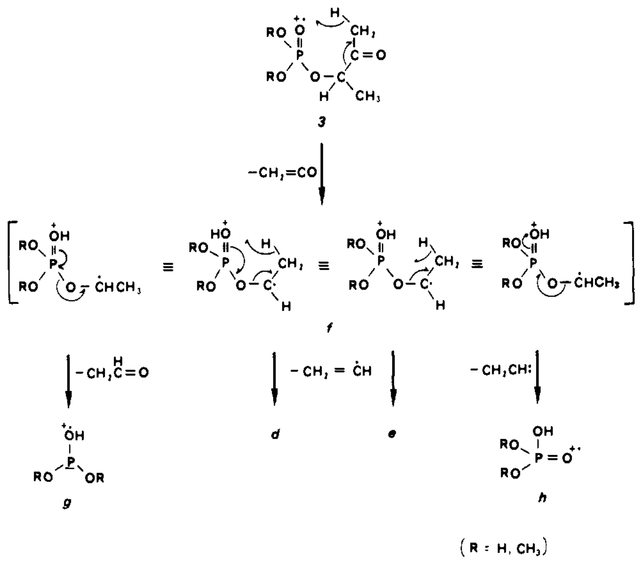
The early stages—to which we propose, for the most part, to limit this discussion—of the chemistry underlying the spectra of both the phosphoacetoins and acetoin acetate are centered in the acetoin group. Primary loss of acetyl radical is prominent in both, presumably reflecting similar consequences, at least in part, of the localized charge and odd electron on an oxygen atom. On the other hand, primary loss of ketene is prominent in the phosphates but plays only a minuscule role in the acetate. This difference would seem to follow from the different geometries of the phosphoryl and carboxyl groups and the consequently different and probably also less specific positional preference in the hydrogen-abstraction step in the former than in the latter. Hydrogen migration in ionic decomposition of aliphatic carbonyl compounds in the mass spectrometer generally favors a six-membered cyclic transition state,[53] and acetoin acetate has no oxygen atom in the appropriate position relative to the methyl hydrogens of either acetyl group. In a two-dimensional representation the phosphoacetoins would seem to be subject to the same limitation, but these compounds proceed along the reaction path with apparent disregard of any such problem.

To help visualize mechanistic details effecting primary loss of $CH_3CO\cdot$, we consider in Scheme III molecular ions with the charge and odd electron localized at three alternative sites: **1**, on the phosphoryl ether oxygen; **2**, on the acetoin carbonyl oxygen; **3**, on the doubly bonded phosphoryl oxygen. In all three representations, loss of $CH_3CO\cdot$ follows readily, but in **3**, unlike **1** and **2**, the process involves a hydrogen-migration step and the resulting product, b, is a protonated vinyl phosphate, an isomer of a, the species obtained from **1** and **2**. Secondary loss of acetaldehyde appears straightforward in a to give c, a protonated or otherwise cationated metaphosphoric acid or methyl metaphosphate, but a path for the equivalent process in b is not readily apparent. Moreover, by analogy with

Scheme III



Scheme IV



dimethyl vinyl phosphate,[54] one would expect b to decompose by losing the $CH_2{=}CHO\cdot$ radical, but our spectra reveal no such process. Hence, we regard the participation of **1** and **2** as plausible but that of **3** as unlikely. The competing secondary reaction of a to lose C_2H_2 requires migration of two hydrogen atoms. To avoid going through a vinyloxy intermediate, which, again, should lose $CH_2{=}CHO\cdot$, we suggest that the first hydrogen migration in a stepwise process occurs from C-1, perhaps to the adjacent oxygen to give a′, paralleling the documented 1,2 migration in the molecular ion of propionitrile.[55] Migration of the second hydrogen atom to either the same ether oxygen or to the doubly bonded phosphoryl oxygen is then followed by loss of vinylidene diradical to give d or e, respectively. Configuration d directly, or e via another hydrogen-migration step, can then eliminate H_2O and complete the second pathway from a to c. The $CH_2{=}C{:}$ configuration for the neutral product of the step a′ → d,e has precedents in other chemical systems and would be expected to reorganize rapidly to acetylene.[56,57a]

A mechanistic formulation to rationalize primary loss of ketene is pictured in Scheme IV. Hydrogen abstraction by the radical site on the doubly bonded phosphoryl oxygen atom in configuration **3** of the molecular ion triggers ketene elimination to yield the radical cation f. A sequence of events that might be directed by the free radical results in the loss of acetaldehyde to yield the phosphorous acid or phosphite ester radical cation g. A second and third sequence, also under the influence of the free radical, effect loss of vinyl radical to contribute to the yield of protonated orthophosphoric acid or phosphate, d and e, which arose also from a different reaction sequence, shown in Scheme III. A fourth sequence, this one directed by the localized charge, effects loss of the ethylidene diradical to yield the orthophosphoric acid or phosphate ester radical cation h. The methyl-substituted carbene $CH_3CH{:}$ is a known species,[57b] which has been identified as a product of the photolysis of methylketene[58] and of ethane.[59] Theoretical calculations[60] indicate that the isomerization $CH_3CH{:} \rightarrow CH_2{=}CH_2$ has virtually no activation energy, in accord with the finding of ethylene as a major stable product of reactions that produce this diradical.[57b,58]

A striking feature of the further decomposition of DMPA and MPAH, but not detected in PAH_2, is the loss of formaldehyde. This reaction is prominent in and appears to be characteristic of the mass spectra of methyl esters of phosphoric and phosphorous and related acids.[7,11,54,61] Thus, migration of a hydrogen atom and elimination of CH_2O is generally the preferred mode of disposing of methoxy groups at numerous points in the ionic decomposition of such esters.

Monomeric Metaphosphate. Finally, in addition to verifying our prior conclusion[5] that MPAH undergoes thermal decomposition to acetoin and methyl metaphosphate, this work has uncovered three new reactions that produce neutral metaphosphoric acid or metaphosphate, further supplementing the list of such examples revealed in a search of the mass-spectral literature.[5] The new reactions consist of (1) the thermolysis of PAH_2 to acetoin and metaphosphoric acid; (2) the thermal dehydration of PAH_2 to acetoin metaphosphate; (3) the EI-induced decomposition of (PAH_2 less $CH_3CO)^+$ to $C_2H_5O^+$ and HPO_3.

Supplementary Material Available: Sample ions unresolved from PFK ions (Table I), EI mass spectra of dimethylphosphoacetoin (Table III), FI mass spectrum of dimethylphosphoacetoin (Table IV), ions of mass greater than 196 in EI mass spectra of dimethylphosphoacetoin (Table V), EI mass spectrum of phosphoacetoin (Table VI), FI mass spectrum of phosphoacetoin (Table VII), a series of FI spectra measured on methylphosphoacetoin (Table X), EI mass spectra of methylphosphoacetoin (Table XI), partial EI mass spectra of methylphosphoacetoin (Table XII), and EI mass spectrum of acetoin acetate (Table XIV) (14 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Standard Oil Company (Indiana). (b) State University of New York at Stony Brook; research supported by Grant GM20672 of the National Institutes of Health.
(2) Lehninger, A. L. "Biochemistry", 2nd ed.; Worth Publishers: New York, 1975; Chapters 16, 23.
(3) Radford, T.; DeJongh, D. C. In "Biochemical Applications of Mass Spectrometry", Waller, G. R., Ed.; Wiley-Interscience: New York, 1972; Chapter 12.
(4) The following abbreviations will be employed: PAH_2, MPAH, and DMPA = phosphoacetoin and its mono- and dimethyl esters: 3-oxo-2-butyl, methyl(3-oxo-2-butyl), and dimethyl(3-oxo-2-butyl) phosphates. Also, EI = electron impact, and FI = field ionization.
(5) Meyerson, S.; Kuhn, E. S.; Ramirez, F.; Marecek, J. F.; Okazaki, H. *J. Am. Chem. Soc.* **1978**, *100*, 4062.
(6) Gillis, R. G.; Occolowitz, J. L. In "Analytical Chemistry of Phosphorus Compounds", Halmann, M., Ed.; Wiley-Interscience: New York, 1972;

Chapter 6.

(7) Granoth, I. *Top. Phosphorus Chem.* **1976,** *8*, 41.

(8) McLafferty, F. W. *Anal. Chem.* **1956,** *28*, 306.

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

(10) Quayle, A. *Adv. Mass Spectrom.* **1959,** *1*, 365.

(11) Bafus, D. A.; Gallegos, E. J.; Kiser, R. W. *J. Phys. Chem.* **1966,** *70*, 2614.

(12) CEC Users' Workshop, Fourth Annual Conference on Mass Spectrometry, Cincinnati, Ohio, 1956.

(13) Cf. also Meyerson, S. *Anal. Chem.* **1956,** *28*, 317.

(14) See: ref 5, footnote 49.

(15) Franklin, W. E. *Anal. Chem.* **1979,** *51*, 992.

(16) Schulten, H.-R.; Beckey, H. D.; Boerboom, A. J. H.; Meuzelaar, H. L. C. *Anal. Chem.* **1973,** *45*, 2358.

(17) (a) Field, F. H.; Franklin, J. L. "Electron Impact Phenomena and the Properties of Gaseous Ions"; Academic Press: New York, 1957; pp 202–204. (b) Beynon, J. H. "Mass Spectrometry and Its Applications to Organic Chemistry"; American Elsevier: New York, 1960; pp 429–430. (c) Cassuto, A. *Adv. Mass Spectrom.* **1963,** *2*, 296. (d) Meyerson, S. *Appl. Spectrosc.* **1968,** *22*, 30.

(18) Hamming, M. C.; Foster, N. G. "Interpretation of Mass Spectra of Organic Compounds"; Academic Press: New York, 1972; p 204.

(19) For a selection of literature examples, see: (a) Cotter, J. L. *J. Chem. Soc.* **1965,** 5742. (b) Waller, G. R.; Ryhage, R.; Meyerson, S. *Anal. Biochem.* **1966,** *16*, 277. (c) Harley-Mason, J.; Toube, T. P.; Williams, D. H. *J. Chem. Soc. B* **1966,** 396. (d) ten Noever de Brauw, M. C.; Brunnée, C. *Z. Anal. Chem.* **1967,** *229*, 321. (e) Ukai, S.; Hirose, K.; Tatematsu, A.; Goto, T. *Tetrahedron Lett.* **1967,** 4999. (f) Oliver, R. W. A.; Rashman, R. M. *J. Chem. Soc. B* **1968,** 1141. (g) Svec, H. J.; Junk, G. A. *Inorg. Chem.* **1968,** *7*, 1688. (h) Kaiser, R. *Chromatographia* **1968,** *1*, 258. (i) Veith, H. J.; Hesse, M. *Helv. Chim. Acta* **1969,** *52*, 2004. (j) Cronin, D. A.; Nursten, H. E.; Woolfe, M. L. *Int. J. Mass Spectrom. Ion Phys.* **1972/73,** *10*, 47.

(20) For a report of particular interest by virtue of being concerned with phosphorus compounds, see: Gara, A. P.; Massy-Westropp, R. A.; Bowie, J. H. *Aust. J. Chem.* **1970,** *23*, 307.

(21) See, for example, (a) Adley, T. J.; Granata, A. *Org. Mass Spectrom.* **1971,** *5*, 365. (b) Budzikiewicz, H.; Linscheid, M. *Biomed. Mass Spectrom.* **1977,** *4*, 103. (c) Helm, A.; Carlsen, L.; Larsen, E. *J. Org. Chem.* **1978,** *43*, 4816.

(22) Beckey, H. D. In ref 3, Chapter 30.

(23) (a) Futrell, J. H.; Ryan, K. R.; Sieck, L. W. *J. Chem. Phys.* **1965,** *43*, 1832. (b) Jennings, K. R. *Ibid.* **1965,** *43*, 4176.

(24) For leading references to early work utilizing metastable peaks to help delineate reaction paths, see: Meyerson, S.; Vander Haar, R. W.; Fields, E. K. *J. Org. Chem.* **1972,** *37*, 4114.

(25) (a) Chupka, W. A. *J. Chem. Phys.* **1959,** *30*, 191. (b) McLafferty, F. W.; Fairweather, R. B. *J. Am. Chem. Soc.* **1968,** *90*, 5915. (c) Williams, D. H.; Cooks, R. G. *Chem. Commun.* **1968,** 663. (d) Brown, P. *Org. Mass Spectrom.* **1970,** *3*, 1175.

(26) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. "Mestastable Ions"; American Elsevier: New York, 1973; (a) p 185; (b) pp 159–172; (c) pp 28–30, 97–101, 225–232, and references cited therein.

(27) Ramirez, F.; Marecek, J. F.; Tsuboi, H.; Chaw, Y. F. *Phosphorus Sulfur* **1978,** *4*, 325.

(28) Ramirez, F.; Marecek, J. F.; Ugi, I. *J. Am. Chem. Soc.* **1975,** *97*, 3809.

(29) Quartz direct-introduction probe purchased from Mass Spectrometer Accessories (College Station, Texas).

(30) See paragraph at end of paper regarding supplementary material.

(31) (a) "Eight Peak Index of Mass Spectra", 2nd ed.; Mass Spectrometry Data Centre: Aldermaston, U.K., 1974; Vol. I, Table 1, p 33, and the original publications from which these data were taken. (b) ASTM Spectrum No. 160. (c) ASTM Spectrum No. 1333. (d) Ferretti, A.; Flanagan, V. P. *J. Agric. Food Chem.* **1971,** *19*, 245.

(32) For a prior exception and a possible alternative explanation, see: Meyerson, S.; Fields, E. K. *Org. Mass Spectrom.* **1974,** *9*, 485.

(33) In mechanistic representations throughout this paper, we follow the practice generally employed in the mass-spectral literature of using a full arrow (↷) to denote shift of a pair of electrons and a fishhook (⌒) for a single electron. For further clarification of this and other aspects of notation associated with gaseous ions, see: Budzikiewicz, H.; Djerassi, C.; Williams, D. H. "Mass Spectrometry of Organic Compounds"; Holden-Day: San Francisco, 1967; pp 1–3.

(34) Brown, P.; Djerassi, C. *Angew. Chem., Int. Ed. Engl.* **1967,** *6*, 477, and references cited therein.

(35) Beckey, H. D. "Principles of Field Ionization and Field Desorption Mass Spectrometry"; Pergamon Press: Elmsford, N.Y., 1977; Chapter 3.

(36) Meyerson, S., unpublished data.

(37) Köppel, C.; Schwarz, H.; Bohlmann, F. *Org. Mass Spectrom.* **1973,** *7*, 875.

(38) Eliel, E. L.; McCollum, J. D.; Meyerson, S.; Rylander, P. N. *J. Am. Chem. Soc.* **1961,** *83*, 2481.

(39) Satterthwait, A.; Westheimer, F. H. *J. Am. Chem. Soc.* **1978,** *100*, 3197.

(40) The previous literature on monomeric metaphosphate species has been reviewed in ref 5 and 41; see also ref 42 and 43 for further evidence in support of the metaphosphate anion in solutions.

(41) Rebek, Jr., J.; Gaviña, F.; Navarro, C. *J. Am. Chem. Soc.* **1978,** *100*, 8113.

(42) Ramirez, F.; Marecek, J. F. *J. Am. Chem. Soc.* **1979,** *101*, 1460.

(43) Ramirez, F.; Marecek, J. F. *Tetrahedron* **1979,** *35*, 1581.

(44) Ramirez, F.; Madan, O. P.; Smith, C. P. *J. Am. Chem. Soc.* **1965,** *87*, 670.

(45) Ramirez, F. *Acc. Chem. Res.* **1968,** *1*, 168.

(46) Van Wazer, J. R. "Phosphorus and Its Compounds", Vol. I; Interscience: New York, 1958; pp 267–279, 692–702.

(47) Ramirez, F.; Ricci, Jr., J. S.; Madan, O. P.; Marecek, J. F.; Tsuboi, H. *J. Am. Chem. Soc.* **1977,** *99*, 5135.

(48) For analogous monomer/dimer contributions to mass spectra of 1-chloro-2-nitrosocycloalkanes, see: Tou, J. C.; Chang, K. Y. *Org. Mass Spectrom.* **1970,** *3*, 1055.

(49) Ranganathan, N.; Brinigar, W. S. *J. Org. Chem.* **1978,** *43*, 4853.

(50) Wood, G. W.; Lau, P.-Y.; Rao, G. N. S. *Biomed. Mass Spectrom.* **1976,** *3*, 172.

(51) Budzikiewicz, H.; Djerassi, C.; Williams, D. H. "Mass Spectrometry of Organic Compounds"; Holden-Day: San Francisco, 1967; (a) pp 9–14; (b) pp 648–651.

(52) For explicit consideration of the concept in various applications, see: (a) Bentley, T. W.; Johnstone, R. A. W.; Mellon, F. A. *J. Chem. Soc. B* **1971,** 1800. (b) Beynon, J. H.; Caprioli, R. M.; Ast, T. *Org. Mass Spectrom.* **1972,** *16*, 273. (c) Fortin, C. J.; Forest, M.; Vaziri, C.; Gravel, D.; Rousseau, Y. *Can. J. Chem.* **1973,** *51*, 3445. (d) Bentley, T. W. In "Mass Spectrometry", Johnstone, R. A. W., Senior Reporter; The Chemical Society: London, 1975; Vol. III, Chapter 2.

(53) (a) McLafferty, F. W. In "Determination of Organic Structures by Physical Methods", Nachod, F. C., Phillips, W. D., Eds.; Academic Press: New York, 1962; Vol. II, Chapter 2. (b) Meyerson, S.; Leitch, L. C. *J. Am. Chem. Soc.* **1971,** *93*, 2244. (c) Kingston, D. G. I.; Bursey, J. T.; Bursey, M. M. *Chem. Rev.* **1974,** *74*, 215.

(54) Gaydou, E. M.; Peiffer, G.; Etienne, M. *Org. Mass Spectrom.* **1974,** *9*, 157.

(55) (a) Meyerson, S.; Karabatsos, G. J. *Org. Mass Spectrom.* **1974,** *8*, 289. (b) Theissling, C. B.; Nibbering, N. M. M.; Meyerson, S. *Ibid.* **1976,** *11*, 838.

(56) Schreck, J. O. *J. Chem. Educ.* **1965,** *42*, 260. (b) Dykstra, C. E.; Schaefer, H. F. *J. Am. Chem. Soc.* **1978,** *100*, 1378. (c) Stang, P. J. *Chem. Rev.* **1978,** *78*, 383. (d) Schaefer, H. F. *Acc. Chem. Res.* **1979,** *12*, 288.

(57) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1964; (a) pp 70–73; (b) pp 47, 50, 60.

(58) Kistiakowsky, G. B.; Mahan, B. H. *J. Am. Chem. Soc.* **1957,** *79*, 2412.

(59) Okabe, H.; McNesby, J. R. *J. Chem. Phys.* **1961,** *34*, 668.

(60) (a) Bodor, N.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1972,** *94*, 9103. (b) Menéndez, V.; Figuera, J. M. *Chem. Phys. Lett.* **1973,** *18*, 426.

(61) (a) Harless, H. R. *Anal. Chem.* **1961,** *33*, 1387. (b) Occolowitz, J. L.; White, G. L. *Ibid.* **1963,** *35*, 1179. (c) Haake, P.; Ossip, P. S. *Tetrahedron* **1968,** *24*, 565. (d) Pritchard, J. G. *Org. Mass Spectrom.* **1970,** *3*, 163. (e) Jakobsen, P.; Treppendahl, S.; Wieczorkowski, J. *Ibid.* **1972,** *6*, 1303. (f) Griffiths, W. R.; Tebby, J. C. *Phosphorus Sulfur* **1978,** *5*, 101.