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The Monomeric Metaphosphate Anion in Negative-Ion Chemical-Ionization Mass Spectra of Phosphotriesters

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Abstract: The monomeric metaphosphate anion, PO_3^-, was first proposed in 1955 as an intermediate in hydrolysis of phosphomonoesters in aqueous solution. But almost a quarter of a century elapsed before its first direct observation, in the negative-ion chemical-ionization (NICI) mass spectra of certain phosphotriesters. To help define the gas-phase reaction paths leading to the formation and subsequent decomposition of PO_3^-, we have studied the NICI spectra of a group of dimethyl vinyl and dimethyl aryl phosphates, employing a variety of mass-spectral experimental techniques. In every case, a (and perhaps *the*) major pathway to PO_3^- appears to consist of the sequence (a) capture of a thermal electron by the molecule, (b) loss of the vinyl or aryl group to produce the dimethyl phosphate anion, and (c) elimination of dimethyl ether to yield PO_3^-. This particle, when suitably activated, decomposes further only by losing an oxygen atom to yield PO_2^-, the metaphosphite anion.

The monomeric metaphosphate anion, PO_3^-, was proposed in 1955 as an intermediate in the hydrolysis of phosphomonoesters in aqueous solution.[2] Numerous studies have been carried out in the hope of establishing the existence of this species.[3,4] Mass spectrometry has demonstrated an impressive capability for detecting and characterizing chemical species that are not isolable in a test tube.[5] This capability arises as a consequence of fairly direct observations on isolated ionized molecules or molecular fragments without the added complications introduced by solvents. We have attempted to exploit this experimental technique in a search for metaphosphate species that might form in the ionization/dissociation of certain phosphate esters and related compounds.[4,6,7] These prior studies, which have been limited to work with positive ions, have uncovered evidence that metaphosphate species occur commonly in both thermal and cationic decompositions of organic phosphates and related molecules in the mass spectrometer. These species arise as neutral molecules in thermal processes and as neutral and protonated or otherwise cationated molecules in cationic processes.[4,6,7]

The present investigation is concerned with attempts to observe the PO_3^- anion in negative-ion (NI) spectra,[8] clearly the logical experimental technique for this purpose. Negative-ion chemical-ionization (NICI)[9] mass spectra of certain organophosphorus pesticides[10] contain prominent peaks of mass[11] 79 that we suspected

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[1] (a) Standard Oil company (Indiana). (b) National Institute of Environmental Health Sciences. (c) State University of New York at Stony Brook.

[2] (a) Butcher, W. W.; Westheimer, F. H. *J. Am. Chem. Soc.* **1955**, *77*, 2420. (b) Barnard, D. W. C.; Bunton, C. A.; Llewellyn, D. R.; Oldham, K. G.; Silver, B. L.; Vernon, C. A. *Chem. Ind.* (*London*) **1955**, 760. (c) Bunton, C. A.; Llewellyn, D. R.; Oldham, K. G.; Vernon, C. A. *J. Chem. Soc.* **1958**, 3574. (d) Bunton, C. A. *Acc. Chem. Res.* **1970**, *3*, 257.

[3] Westheimer, F. H. *Chem. Rev.* **1981**, *81*, 313.

[4] For a review of monomeric metaphosphoric acid derivatives in mass spectra, see: Meyerson, S.; Kuhn, E. S.; Ramirez, F.; Marecek, J. F.; Okazaki, H. *J. Am. Chem. Soc.* **1978**, *100*, 4062.

[5] See, for example: (a) Meyerson, S.; Corbin, J. L. *J. Am. Chem. Soc.* **1965**, *87*, 3045. (b) Kirk, R. W.; Timms, P. L. *Chem. Commun.* **1967**, 18. (c) Bursey, M. M.; Cerny, R. L.; Pedersen, L. G.; Gottschalk, K. E.; Tomer, K. B.; Lehman, T. A. *J. Chem. Soc., Chem. Commun.* **1983**, 517. (d) Kleingeld, J. C.; Ingemann, S.; Jalonen, J. E.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1983**, *105*, 2474. (e) Halim, H.; Schwarz, H.; Terlouw, J. K.; Levsen, K. *Org. Mass Spectrom.* **1983**, *18*, 147. (f) Albrecht, B.; Allan, M.; Haselbach, E.; Neuhaus, L.; Carrupt, P.-A. *Helv. Chim. Acta* **1984**, *67*, 220.

[6] Meyerson, S.; Kuhn, E. S.; Ramirez, F.; Marecek, J. F.; Okazaki, H. *J. Am. Chem. Soc.* **1980**, *102*, 2398.

[7] Meyerson, S.; Kuhn, E. S.; Ramirez, F.; Yemul, S. S.; Marecek, J. F. *Tetrahedron*, in press.

[8] We are indebted to F. E. Saalfeld, Naval Research Laboratory, Washington, DC, for first suggesting this approach to us.

[9] For recent reviews, see: (a) Bowie, J. H.; Williams, B. D. In "International Review of Science. Physical Chemistry Series Two. Mass Spectrometry"; Maccoll, A., Ed.; Butterworths: London, 1975; Vol. 5, Chapter 3. (b) Jennings, K. R. In "Specialist Periodical Report. Mass Spectrometry"; The Chemical Society: London, 1977; Chapter 9. (c) Jennings, K. R. *Philos. Trans. R. Soc. London, Ser. A* **1979**, *A293*, 125. (d) Field, F. H., paper presented at the American Society Mass Spectrometry, 28th Annual Conference on Mass Spectrometry and Allied Topics, New York, 1980. (e) Budzikiewicz, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 624. (f) Dougherty, R. C. *Anal. Chem.* **1981**, *53*, 625A.

[10] Busch, K. L.; Bursey, M. M.; Hass, J. R.; Sovocool, G. W. *Appl. Spectrosc.* **1978**, *32*, 388.

[11] Use of the simpler term "mass" rather than the usual "mass-to-charge ratio" (*m*/*z*) introduces no ambiguity because *z* is equal to unity throughout this work.

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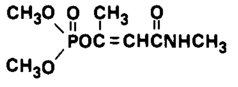
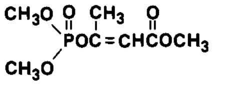
might be attributable to the PO_3^- ion. Exact mass measurements, reported in a preliminary communication,[12] showed that 99.9% of the ion current at mass 79 in the NICI spectra of Monocrotophos (**1**) and Mevinphos (**2**) was indeed carried by the PO_3^- anion. We have now carried out further work in an attempt to clarify the anionic gas-phase reaction paths that lead to PO_3^- from the vinyl phosphotriesters **1** and **2** and to explore additional aspects of the chemistry underlying NICI spectra of phosphate esters. We have included in the study the spectra of a series of aryl dimethyl phosphates: dimethyl phenyl (**3**), dimethyl 4-nitrophenyl (**4**), and dimethyl 2,4-dinitrophenyl (**5**) phosphates.



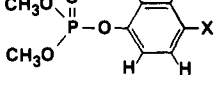
$(CH_3O)_2P(O)OC(CH_3)=CHC(O)NHCH_3$

1



$(CH_3O)_2P(O)OC(CH_3)=CHC(O)OCH_3$

2



3 X = Y = H

4 X = NO_2, Y = H

5 X = Y = NO_2

The behavior in solution of the aryl phosphates, $ArOP(O)(OH)_2$, related to **3**–**5**, has been the subject of recent studies.[13] In solution, the unprotonated species, $ArOPO_3^{2-}$, appear generally to undergo substitutions by the elimination–addition mechanism, that is, via a PO_3^- intermediate. The monoprotonated species, $ArOPO_3H^-$, are capable of reacting either by elimination–addition or by addition–elimination, apparently under the control of electronic considerations determined by the number of nitro groups on the phenyl ring. As will be described below, we find that the number of nitro groups also has a pronounced effect on the NI mass spectra of the dimethyl aryl esters.

A literature search on NI mass spectra of organophosphorus pesticides revealed, in addition to the work cited [10,12] and an earlier paper,[14] new reports[15,16] published while the present study was in progress. One of these[15] includes spectra of **1** and **2**, which consist of only two peaks and one peak, respectively (peaks of relative intensity <5% were not reported): for **1**, peaks at mass 125, relative intensity 100, attributed to $(CH_3O)_2PO_2^-$, and 208, relative intensity 9, attributed to loss of $\cdot CH_3$ from the molecular radical anion; for **2**, only a peak at mass 125, also attributed to $(CH_3O)_2PO_2^-$. Many of the compounds dealt with in these reports are phospho- (or mono- or dithiophospho-) triesters and, as with other phosphotriesters,[17-21] their NI spectra are generally dominated by loss of an alkyl or aryl group to produce a phosphate monoanion; for the most part, they show little or no PO_3^-. Also while the present study was underway, occurrence of the PO_3^- ion over a range of abundance levels was reported in NI mass spectra of several phosphate esters, obtained by a variety of techniques—^{252}Cf plasma desorption,[22,23] secondary ion mass spectrometry,[24,25] laser desorption,[26] liquid ion evaporation,[27] fast atom bombardment,[28] and direct chemical ionization[29] —and presumably reflecting the different levels of excitation introduced by the different means of ionization. In one[27] of these reports the conventionally measured spectrum showed no PO_3^-, but this ion, accompanied by adenosine diphosphate monoanion, was produced in good yield by collision-induced decomposition (CID) of the adenosine 5′-triphosphate dianion; the decomposition appears to proceed precisely in accord with the postulated elimination step of the elimination–addition mechanism in basic solution.[30] In only one report[22] was the peak assignment to PO_3^- confirmed by exact mass measurement.

The above data are in accord with the observation that NI spectra generally are much simpler than their positive-ion (PI) counterparts. Spontaneous decomposition is likely to proceed via fewer and shorter reaction paths because in those anions that contain sufficient energy decomposition must compete with autodetachment, that is, reversion to a neutral molecule and an electron.[9,31] In addition, as in PI spectra, ions formed in the source at the comparatively high pressures employed in CI mass spectrometry may dispose of excess energy via collisional deactivation.[9,32] The resulting spectral simplicity implies also low informational content, but this can generally be compensated for by the use of scanning modes that take advantage of either spontaneous or collision-induced decompositions in selected segments of the ion-flight path.[33] Although these techniques have been employed chiefly to study cationic processes, a number of literature reports in addition to the one referred to above[27] demonstrate their applicability to anionic processes as well.[34] In particular, we have used the technique of mass-analyzed ion kinetic energy spectroscopy (MIKES) coupled with CID.[33] An ion beam of selected mass, isolated via the magnetic analyzer of a mass spectrometer of reversed geometry, is induced to decompose by passage through a gas cloud in a collision chamber, and the resultant charged fragments are then sorted by the electrical analyzer to yield a mass spectrum of decomposition products derived from the original selected ion beam.

Our work included exact mass measurement as a basis for assigning ion compositions. We used perfluorokerosene to calibrate the mass scale,[17,35] supplemented when necessary by peak matching.

Experimental Section

Materials. The pesticides Mevinphos (Phosdrin; alpha isomer 65%) and Monocrotophos (Azodrin) were received from the U.S. E.P.A.

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[12] Harvan, D. J.; Hass, J. R.; Busch, K. L; Bursey, M. M.; Ramirez, F.; Meyerson, S. *J. Am. Chem. Soc.* **1979**, *101*, 7409.

[13] (a) Ramirez, F.; Marecek, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 1460. (b) Ramirez, F.; Marecek, J. F. *Tetrahedron* **1979**, *35*, 1581. (c) Ramirez, F.; Marecek, J. F. *Tetrahedron* **1980**, *36*, 3151. (d) Ramirez, F.; Marecek, J. F. *Pure Appl. Chem.* **1980**, *52*, 1021.

[14] Rankin, P. C. *J. Assoc. Off. Anal. Chem.* **1971**, *54*, 1340.

[15] Stan, H.-J.; Kellner, G. *Biomed. Mass Spectrom.* **1982**, *9*, 483. See also: Stan, H.-J.; Kellner, G. In "Recent Developments in Food Analysis"; Baltes, W., Czedik-Eysenberg, P. B., Pfannhauser, W., Eds.; Verlag Chemie: Weinheim, Germany, 1982; p 183.

[16] Safe, S. H.; Boyd, R. K. In "Pesticide Analysis"; Das, K. G., Ed.; Marcel Dekker: New York, 1981; Chapter 8.

[17] Large, R.; Knof, H. *Org. Mass Spectrom.* **1976**, *11*, 582.

[18] Meyer, H. J.; Larsson, F. C. V.; Lawesson, S.-O.; Bowie, J. H. *Bull. Soc. Chim. Belg.* **1978**, *87*, 517.

[19] Dougherty, R. C.; Wander, J. D. *Org. Mass Spectrom.* **1980**, *7*, 401.

[20] Brandenberger, H. *Recent Dev. Mass Spectrom. Biochem. Med.* **1980**, *6*, 391.

[21] McNeal, C. J.; Ogilvie, K. K.; Theriault, N. Y.; Nemer, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 972.

[22] Chait, B. T.; Agosta, W. C.; Field, F. H. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 339.

[23] McNeal, C. J.; Ogilvie, K. K.; Theriault, N. Y.; Nemer, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 976.

[24] Eicke, A.; Sichtermann, W.; Benninghoven, A. *Org. Mass Spectrom.* **1980**, *15*, 289.

[25] Ens, W.; Standing, K. G.; Westmore, J. B.; Ogilvie, K. K.; Nemer, M. J. *Anal. Chem.* **1982**, *54*, 960.

[26] Hercules, D. M.; Day, R. J.; Balasanmugam, K.; Dang, T. A.; Li, C. P. *Anal. Chem.* **1982**, *54*, 280A.

[27] Thomson, B. A.; Iribarne, J. V.; Dziedzic, P. J. *Anal. Chem.* **1982**, *54*, 2219.

[28] Sindona, G.; Uccella, N.; Weclawek, K. *J. Chem. Res. Synop.* **1982**, 184.

[29] Bruins, A. P., private communication.

[30] (a) Meyerson, S.; Kuhn, E. S.; Ramirez, F.; Marecek, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 7231. (b) Miller, D. L.; Westheimer, F. H. *J. Am. Chem. Soc.* **1966**, *88*, 1507.

[31] Christophorou, L. G. *Adv. Electron. Electron Phys.* **1978**, *46*, 55.

[32] Szulejko, J. E.; Howe, I.; Beynon, J. H.; Schlunegger, U. P. *Org. Mass Spectrom.* **1980**, *15*, 263.

[33] For a recent review and leading references, see: Schlunegger, U. P. *Top. Curr. Chem.* **1981**, *95*, 49.

[34] See, for example: (a) Donnally, B. L.; Carr, H. E. *Phys. Rev.* **1954**, *93*, 111. (b) Bowie, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 5795. (c) Bowie, J. H.; Hart, S. G. *Int. J. Mass Spectrom. Ion Phys.* **1974**, *13*, 319. (d) Bowie, J. H. *EHP, Environ. Health Perspect.* **1980**, *36*, 89. (e) Bambagiotti, M.; Giannellini, V.; Coran, S. A.; Vincieri, F. F.; Moneti, G.; Selva, A.; Traldi, P. *Biomed. Mass Spectrom.* **1982**, *9*, 495.

[35] (a) The earliest suggestion, to our knowledge, of using this means of mass-marking NI spectra was made in a private communication from R. C. Dougherty, Florida State University, to S. Evans, Kratos, on the basis of unpublished work by the former in 1966. (b) Gohlke, R. S.; Thompson, L. H. *Anal. Chem.* **1968**, *40*, 1004. (c) Bruins, A. P. *Biomed. Mass Spectrom.* **1980**, *7*, 454.

Table I. NICI Spectrum of Monocrotophos (**1**)

mass	rel intensity	probable ion composition[a]	relationship to M, the original molecule
348[b]	<0.4	$C_9H_{20}NO_9P_2^-$	$(M + C_2H_6O_4P)^-$
222[b]	<0.1	$C_7H_{13}NO_5P^-$	$(M - H)^-$
208	0.2	$C_6H_{11}NO_5P^-$	$(M - CH_3)^-$
176	0.1	$C_5H_7NO_4P^-$	$(M - C_2H_7O)^-$
127	0.7	$C_2H_6{}^{18}OO_3P^-$	
126	2	$^{13}CCH_6O_4P^-$	
125	100	$C_2H_6O_4P^-$	$(CH_3O)_2PO_2^-$
124	0.6	$C_2H_5O_4P^{-\cdot}$	$(125 - H)^{-\cdot}$
114	0.1	$C_5H_8NO_2^-$	$(M - (CH_3O)_2PO)^- = CH_3NHCOCH{=}C(CH_3)O^-$
79	0.4	O_3P^-	
63	0.02	O_2P^-	

[a] Inferred from exact mass measurement. [b] Observed only in scans in which ion current at mass 125 was great enough to overload, and hence block, the amplifier. Limiting intensity shown is an estimate obtained by proportioning to intensity at mass 208.

Table II. NICI Spectrum of Mevinphos (**2**)

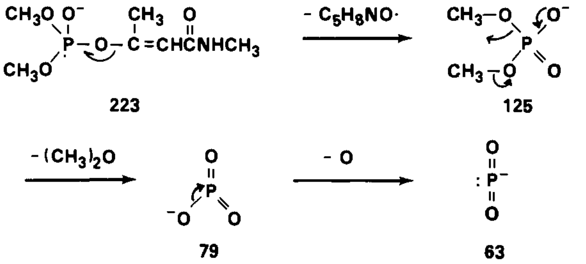
mass	rel intensity	probable ion composition[a]	relationship to M, the original molecule
251[b]	<2	$C_4H_{13}O_8P_2^-$	$(2(CH_3O)_2PO_2 + H)^-$
246	2	$C_9H_{11}O_6P^{-\cdot}$	impurity
218	1	$C_8H_{11}O_5P^{-\cdot}$	impurity
210[c]	0.2	$C_6H_{11}O_6P^{-\cdot}$	impurity
209[d]	0.1	$C_6H_{10}O_6P^-$	$(M - CH_3)^-$, $(210 - H)^-$
195	0.4	$C_5H_8O_6P^-$	$(210 - CH_3)^-$
151	0.4	$C_4H_8O_4P^-$	$(M - C_3H_5O_2)^-$
127	1	$C_2H_6{}^{18}OO_3P^-$	
126	3	$^{13}CCH_6O_4P^-$	
125	100	$C_2H_6O_4P^-$	$(CH_3O)_2PO_2^-$
124	0.4	$C_2H_5O_4P^{-\cdot}$	$(125 - H)^{-\cdot}$
111	1	$CH_4O_4P^-$	$(CH_3O)(HO)PO_2^-$
79	0.1	O_3P^-	

[a] See footnote *a*, Table I. [b] See footnote *b*, Table I. Limiting intensity shown is an estimate obtained by proportioning to intensity at mass 195. [c] This may be the molecular radical anion of a compound differing from **2** only in having one methoxy group replaced by an acidic hydroxy group. [d] Intensity increased sharply under conditions described in footnote *b*, indicating a contribution from a bimolecular reaction product.

Table III. Exact Mass Measurements on Mevinphos (**2**) and the Inferred Elemental Compositions

measured mass	assignment	
	formula	mass
251.0089	$C_4H_{13}O_8P_2^-$	251.0086
246.0297	$C_9H_{11}O_6P^{-\cdot}$	246.0293
218.0339	$C_8H_{11}O_5P^{-\cdot}$	218.0345
210.0302	$C_6H_{11}O_6P^{-\cdot}$	210.0293
209.0214	$C_6H_{10}O_6P^-$	209.0215
195.0055	$C_5H_8O_6P^-$	195.0058
151.0165	$C_4H_8O_4P^-$	151.0160
127.0036	$C_2H_6{}^{18}OO_3P^-$	127.0046
126.0054	$^{13}CCH_6O_4P^-$	126.0037
125.0015	$C_2H_6O_4P^-$	125.0004
123.9931	$C_2H_5O_4P^{-\cdot}$	123.9925
110.9821	$CH_4O_4P^-$	110.9847
78.9590	O_3P^-	78.9585

Scheme I



Pesticides and Industrial Chemical Repository (Research Triangle Park, NC 27711) and were used without further purification.

Dimethyl Phenyl Phosphate. A solution of phenyl phosphorodichloridate (42.2 g; 0.2 mol) in anhydrous ether (250 mL) was treated at 0 °C with a solution of methanol (12.8 g; 0.40 mol) and triethylamine (40.4 g; 0.4 mol) in ether (50 mL), with stirring. After 1 h, the mixture was filtered and the solvent was evaporated in vacuum. The ester[36] was purified by vacuum distillation; yield 24.6 g (61%); ^{31}P δ −4.0 (to high field of H_3PO_4 = 0, in $CDCl_3$).

Dimethyl 4-Nitrophenyl Phosphate. A mixture of 4-nitrophenol (7.64 g; 0.055 mol) and triethylamine (5.56 g; 0.055 mol) in anhydrous ether (40 mL) was added, over a 30-min period, to a solution of methyl phosphorodichloridate (7.96 g; 0.055 mol) in ether (40 mL) at 25 °C, with stirring. After 1 h at 25 °C, the mixture was filtered. The solid salt was washed with ether. The combined ether solution was kept 12 h at 5 °C, and the mixture was filtered. The filtrate was evaporated under vacuum to yield the ester[37] as a yellow oil, not purified further; yield 13.1 g (96%); ^{31}P $\delta = -4.8$ (in $CDCl_3$).

Dimethyl 2,4-Dinitrophenyl Phosphate. 2,4-Dinitrophenyl phosphate was prepared as previously described.[38] An ether solution (10 mL) of the acid (0.32 g) was treated with an excess of diazomethane in ether. The ether and excess diazomethane were evaporated and the residue was kept several h at 0.5 torr (20 °C) to yield the ester[39] as an oil in nearly theoretical yield; ^{31}P δ −5.6 (in $CDCl_3$).

Mass Spectrometry. The methane-enhanced negative-ion mass spectra were acquired on a VG ZAB-2F mass spectrometer with a Finnigan-Incos 2300 data system. The mass spectrometer was operated at 7-kV accelerating voltage, 100-μA trap current, 200 °C source temperature, and 3×10^{-5} torr methane gauge pressure (approximately 0.05–0.1 torr in the source block).[40] For CID-MIKES scans, the instrument was operated at mass resolution of 1000, with helium as the collision gas at a gauge pressure of 2×10^{-7} torr. For exact mass measurements, the instrument was operated at 10 000 resolution, with perfluorokerosene as internal standard. Samples were introduced by direct probe. For the high-voltage precursor scans, the daughter ion of interest was focused at 3 kV, the magnetic field and electric-analyzer field fixed, and the high voltage scanned from 2 to 8.5 kV. In all spectra reported here, the intensity scale is defined by assigning a value of 100 to the most intense peak.

Results

The methane-enhanced NICI spectra of vinyl phosphates **1** and **2** are listed in Tables I and II. Table III shows the exact mass measurements for compound **2**, to illustrate their use for assigning elemental compositions of ions. Replicate spectra measured over a period of several months are in generally good agreement. Variations in weaker peak intensities presumably reflect undefined differences in source temperature and surface conditions, in the pressure of methane and the compound under study, and in the levels of adventitious trace oxygen and water that may have been incompletely removed by pumping or introduced as impurities in the methane.[42,43]

In accordance with present views on the formation of negative ions when methane is the moderating gas, we assume that the ions in Tables I and II are produced as a result of the attachment of an electron to the ester molecule. The resulting molecular radical anions in both esters **1** and **2** lose the vinyl group in the predom-

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(36) Mathieson, D. W.; Russell, D. W. *J. Pharm. Pharmacol.* **1957**, *9*, 612.

(37) de Roos, A. M.; Toef, H. J. *Recl. Trav. Chim. Pays-*Bas **1958**, *77*, 946.

(38) Ramirez, F.; Marecek, J. F. *Synthesis* **1978**, 601.

(39) Pocker, Y.; Sarkanen, S. *Biochemistry* **1978**, *17*, 1110.

(40) For calibration purposes, pressures in the source were measured with an MKS Baratron capacitance manometer. For a given gauge pressure, source pressure varies a little from one source to another. The ratio between source pressure and gauge pressure, ~ 2×10^3, is close to the values reported by other workers.[32,41,42]

(41) (a) Stöckl, D.; Budzikiewicz, H. *Org. Mass Spectrom.* **1982**, *17*, 376. (b) Yinon, J.; Laschever, M. *Eur. J. Mass Spectrom.* **1982**, *2*, 101.

(42) Garland, W. A.; Miwa, B. J. *Biomed. Mass Spectrom.* **1983**, *10*, 126.

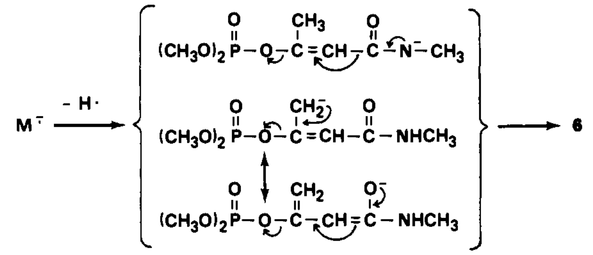
(43) Compare: (a) Dougherty, R. C.; Weisenberger, C. R. *J. Am. Chem. Soc.* **1968**, *90*, 6570. (b) Levonowich, P. F.; Tannenbaum, H. P.; Dougherty, R. C. *J. Chem. Soc., Chem. Commun.* **1975**, 597. (c) Brumley, W. C.; Nesheim, S.; Trucksess, M. W.; Trucksess, E. W.; Dreifuss, P. A.; Roach, J. A. G.; Andrzejewski, D.; Eppley, R. M.; Pohland, A. E.; Thorpe, C. W.; Sphon, J. A. *Anal. Chem.* **1981**, *53*, 2003.

Table IV. CID-MIKE Spectra of Selected Ions in the NICI Spectrum of Monocrotophos (**1**)

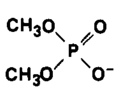
mass scanned	daughter-ion masses found	rel intensity
348	125	100[a]
222	125	100[a]
208	207	31[b]
	149	26
	114	16
	111	100
	79	19
176	160	12[b]
	111	100
	82	59
	79	25
125	124	100[c]
	110	42
	94	16
	79	24
114	113	44[b]
	72	16
	57	100

[a] Peaks of relative intensity <0.5 are omitted. [b] Peaks of relative intensity <10 are omitted. [c] Peaks of relative intensity <5 are omitted.

Scheme II



inating pathway. This process yields the dimethyl phosphate anion, **6**, which comprises >90% of the total ion yield in both spectra.



6, Mass 125

The cluster ion of mass 348 in the spectrum of **1**, which is observed only when sample pressure is high enough that the amplifier is overloaded by the ion current at mass 125, presumably arises by attachment of anion **6** to a molecule of **1** (see Discussion).

The observations described below suggest that the principal reaction pathway leading to formation of the metaphosphate ion, PO_3^-, and its subsequent decomposition into the metaphosphite ion, PO_2^-, starts with loss of the vinyl group from the molecular radical anion, as shown in Scheme I (the numerical values accompanying the formulas denote their nominal masses). We picture the major primary process as homolytic cleavage of a carbon–oxygen bond, with the driving force derived from the stability of the dimethyl phosphate anion. The total absence of $M^{-}\cdot$ in the NICI spectra of four of the five phosphates we studied implies that decomposition of $M^{-}\cdot$ is very fast, and if this decomposition is essentially complete in $\leq 10^{-6}$ s, a metastable-scan search for precursors of m/z 125 will not show $M^{-}\cdot$ regardless of how large a role it plays.

A second, presumably minor, pathway to the dimethyl phosphate anion **6** is supported by the CID-MIKE peak in Table IV for the reaction step $222^- \rightarrow 125^- + 97$. As pictured in Scheme II, this represents a stepwise decomposition of the molecular radical anion to the dimethyl phosphate anion through one or more intermediates of composition $(M - H)^-$, i.e., even-electron anions.

An accelerating-voltage metastable scan[33] on the PO_3^- peak in the spectrum of **1** yields peaks for two precursors, of masses 125 and 111, with relative intensities of 100 and 19, respectively. A MIKE scan on the PO_3^- peak, at nominal pressure of 2×10^{-8} torr, with no collision gas added, shows no decomposition products (the pressure was measured on an ionization gauge in the pumping line that evacuates the second field-free region and the collision chamber located there). Similar scans with added collision gas to nominal pressures of 5×10^{-8}, 1×10^{-7}, 4×10^{-7}, and 1×10^{-6} torr all reveal one product, PO_2^-. Thus, this pathway leads to both the metaphosphate and metaphosphite anions via the dimethyl phosphate anion, **6**.

Table V. CID-MIKE Spectra of Selected Ions in the NICI Spectrum of Mevinphos (**2**)

mass scanned	daughter-ion masses found	rel intensity[a]
209	125	100
	111	9
125	124	100
	110	34
	94	12
	79	17
111	110	10
	96	13
	79	100

[a] See footnote *c*, Table IV.

Table VI. Ions of Nominal Mass 79 in the NICI Spectra of Dimethyl Aryl Phosphates **3**, **4**, and **5**

anion[a]	rel intensity		
	3	**4**	**5**
Br^-	1.9	1.8	2.8
PO_3^-	100.0	100.0	100.0
$CH_4PO_2^-$	0.4	0.1	
$C_4HNO^{-}\cdot$		0.2	15.6
$C_5H_3O^-$			19.3

[a] See footnote *a*, Table I.

Table IV lists the spectra obtained by CID-MIKES of the ions of masses 348, 222, 208, 176, 125, and 114 in the NICI spectrum of **1**.

An accelerating-voltage metastable scan on the PO_3^- peak in the spectrum of **2** is essentially indistinguishable from that obtained from **1**. It yields peaks at masses 125 and 111, with relative intensities of 100 and 21, respectively. A CID-MIKE scan on the PO_3^- peak again yields but one product, PO_2^-.

Table V lists the spectra obtained by CID-MIKES of the ions of masses 209, 125, and 111 in the NICI spectrum of **2**.

Prior to an examination of the NICI spectra of the aryl dimethyl phosphates, **3**–**5**, we sought assurance of the presence of a PO_3^- peak. Exact mass measurements confirmed PO_3^- as the most abundant ion of nominal mass 79, but it was accompanied by other anions in all three spectra, most prominently in that of **5**. Table VI lists the ions so found. The C_4HNO^- and $C_5H_3O^-$ ions in the spectrum of **5**, which are clearly fragments derived from the aryloxy group, constituted our first hint that a dinitrophenoxy group plays a more prominent role than phenoxy or mononitrophenoxy in the NI mass spectra of these esters. Like other features of the spectra to be discussed below, these ions reflect an increasing tendency with increasing extent of nitration for the aryloxy group to compete with the phosphoryl group for the negative charge.

The NICI spectra of the aryl dimethyl phosphates, **3**–**5**, are listed in Tables VII, VIII, and IX, respectively. Table X shows the accelerating-voltage metastable-scan spectra of the mass 79 ion beam in the NICI spectra of the three esters; CID-MIKE scans of this ion beam derived from all three esters showed only one product, PO_2^-, the same as observed with the vinyl phosphates **1** and **2**.

To clarify the decomposition reactions underlying the spectra, we recorded CID-MIKE spectra of the more abundant fragment ions that form from each of the dimethyl aryl phosphates. The spectra are listed in Tables XI, XII, and XIII.

Table VII. NICI Spectrum of Dimethyl Phenyl Phosphate (**3**)

mass	rel intensity[a]	probable ion composition[b]	relationship to M, the original molecule
202	0.3[c]	$C_8H_{11}O_4P^{-}\cdot$	$M^{-}\cdot$
201	0.2[c]	$C_8H_{10}O_4P^{-}$	$(M - H)^{-}$
187	5	$C_7H_8O_4P^{-}$	$(M - CH_3)^{-}$
126	1	$^{13}CCH_6O_4P^{-}$	
125	100	$C_2H_6O_4P^{-}$	$(M - C_6H_5)^{-} = (CH_3O)_2PO_2^{-}$
107	1	$C_7H_7O^{-}$	$(C_6H_5O + CH_2)^{-}$
93	20	$C_6H_5O^{-}$	$(M - (CH_3O)_2PO)^{-}$
79	15	O_3P^{-}	
63	5	O_2P^{-}	

[a] See footnote *a*, Table IV. [b] See footnote *a*, Table I. [c] Not detected in the scan listed here, but observed occasionally in other scans at about the level shown.

Table VIII. NICI Spectrum of Dimethyl 4-Nitrophenyl Phosphate (**4**)

mass	rel intensity[a]	probable ion composition[b]	relationship to M, the original molecule
247	4	$C_8H_{10}NO_6P^{-}\cdot$	$M^{-}\cdot$
232	1[c]	$C_7H_7NO_6P^{-}$	$(M - CH_3)^{-}$
139	3	$^{13}CC_5H_4NO_3^{-}$	
138	21	$C_6H_4NO_3^{-}$	$(M - (CH_3O)_2PO)^{-} = O_2NC_6H_4O^{-}$
126	2	$^{13}CCH_6O_4P^{-}$	
125	100	$C_2H_6O_4P^{-}$	$(M - C_6H_4NO_2)^{-} = (CH_3O)_2PO_2^{-}$
124	18	$C_2H_5O_4P^{-}\cdot$	$(125 - H)^{-}\cdot$
79	1[c]	PO_3^{-}	
46	1[c]	NO_2^{-}	

[a] See footnote *a*, Table IV. [b] See footnote *a*, Table I. [c] See footnote *c*, Table VII.

Table IX. NICI Spectrum of Dimethyl 2,4-Dinitrophenyl Phosphate (**5**)

mass	rel intensity[a]	probable ion composition[b]	relationship to M, the original molecule
184	1	$^{13}CC_5H_3N_2O_5^{-}$	
183	27	$C_6H_3N_2O_5^{-}$	$(M - (CH_3O)_2PO)^{-} = (O_2N)_2C_6H_3O^{-}$
168	5	$^{13}CC_5H_3N_2O_4^{-}$	
167	100	$C_6H_3N_2O_4^{-}$	$(M - (CH_3O)_2PO_2)^{-} = (O_2N)_2C_6H_3^{-}$
153	1	$C_6H_5N_2O_3^{-}$	see text
137	11	$C_6H_3NO_3^{-}\cdot$	$183^{-} - NO_2\cdot$
125	7	$C_2H_6O_4P^{-}$	$(M - (O_2N)_2C_6H_3)^{-} = (CH_3O)_2PO_2^{-}$

[a] See footnote *a*, Table IV. [b] See footnote *a*, Table I.

Table X. Accelerating-Voltage Metastable Scans on Mass 79 Peak in the NICI Spectra of Dimethyl Aryl Phosphates

precursor found		rel intensity[a]		
mass	ion	**3**	**4**	**5**
201	$C_8H_{10}O_4P^{-}$	1		
187	$C_7H_8O_4P^{-}$	5		
183	$C_6H_3N_2O_5^{-}$			28
153	$C_6H_5N_2O_3^{-}$			9
137	$C_6H_3NO_3^{-}\cdot$			7
125	$C_2H_6O_4P^{-}$	100	100	100
111	$CH_4O_4P^{-}$	22	17	22

[a] See footnote *a*, Table IV.

Discussion

The data reported here furnish a satisfactory basis for constructing mechanistic schemes to account for the spectra. Following Alexander, Bigley, and Todd,[44] we picture the newly captured thermal electron as localized on an electronegative group or atom in the molecule, preferably on the positive end of a dipole. The resulting phosphoranyl radical anion breaks down to yield PO_3^{-} chiefly via a dimethyl phosphate anion intermediate in the spectrum of each of the five compounds studied here. Our data

Table XI. CID-MIKE Spectra of Selected Ions in the NICI Spectrum of Dimethyl Phenyl Phosphate (**3**)

mass scanned	daughter-ion masses found	rel intensity[a]
201	155	5
	139	8
	125	100
	94	3
	79	3
	63	3
187	186	100
	172	2
	155	2
	93	48
	79	20
	63	2
125	124	100
	110	26
	94	5
	79	10
	63	1

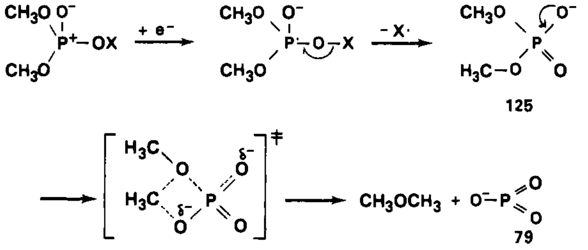
[a] See footnote *a*, Table IV.

Table XII. CID-MIKE Spectra of Selected Ions in the NICI Spectrum of Dimethyl 4-Nitrophenyl Phosphate (**4**)

mass scanned	daughter-ion masses found	rel intensity[a]
247	246	8
	232	3
	138	8
	125	100
232	138	100
201	200	30
	155	4
	125	100
	94	12
	79	12
138	137	100
	122	1
	108	31[b]
	107	23[b]
	92	3[b]
	91	1[b]
	46	3
125	124	100
	110	46
	94	10
	79	20
	63	1
124	123	82
	94	100
	79	52
	63	1

[a] See footnote *a*, Table IV. [b] Incompletely resolved.

Scheme III



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[44] Alexander, R. G.; Bigley, D. B.; Todd, J. F. J. *Org. Mass Spectrom.* **1973**, *7*, 643.

Table XIII. CID-MIKE Spectra of Selected Ions in the NICI Spectrum of Dimethyl 2,4-Dinitrophenyl Phosphate (**5**)

mass scanned	daughter-ion masses found	rel intensity[a]
183	182	28
	167	22
	153	12
	137	100
	123	7
	109	18
	95	4
	79	4
	65	1
	51	1
	46	5
167	137	100
	121	1
	109	17
125	124	100
	110	16
	94	7
	79	14
	63	2
	51	4

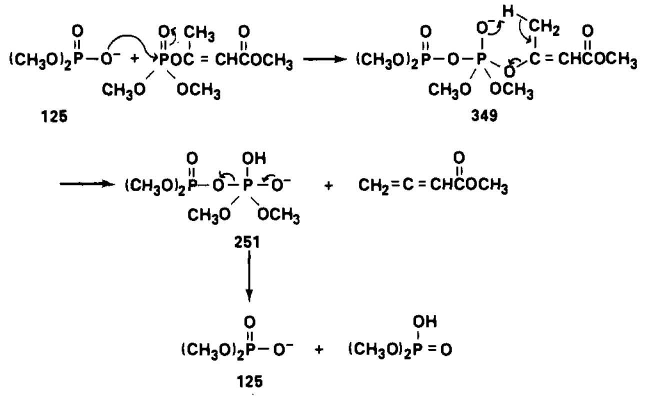
[a] See footnote *a*, Table IV.

do not define the relative extents to which the dimethyl phosphate anion arises in a single step by homolytic carbon–oxygen bond cleavage, as shown in Scheme III, and by heterolytic cleavage of an even-electron intermediate formed by homolysis of an allylic carbon–hydrogen or amide nitrogen–hydrogen bond, as illustrated in Scheme II. Accelerating-voltage scans were made on the mass 125 ion beam of each of the five esters to identify precursors, but in no case did we find a peak clearly attributable to the molecular anion. If the molecular anion is indeed the major precursor, as we postulate, primary loss of X· (Scheme III) appears to be fast enough that it is essentially complete before the ions leave the source, and hence is not detected in metastable scans. Accelerating-voltage scans record the products of decompositions occurring in the first field-free region, after acceleration but before entering the magnetic analyzer. These scans reveal one precursor each in the cases of vinyl phosphate **1** and aryl phosphates **3**–**5**, and none for vinyl phosphate **2**. For **1**, **3**, and **4**, the precursor so found appears to be $(M - H)^-$; for **5**, an anion of mass 250 was found. For **1** and **3**, this finding follows also from the complementary CID-MIKE spectra of $(M - H)^-$ (see Tables IV and XI). In view of the low resolution associated with accelerating-voltage scans, however, we cannot rule out unresolved contributions from $M^{-\cdot}$, the molecular radical anions, as well, as observed, in fact, in the CID-MIKE spectrum of mass 247 from **4** (see Table XII). For the same reason, we suspect that the precursor mass from **5** may actually be not 250 but 251. This ion, observed in NICI spectra of **2** under higher than normal sample presure (see Table II), was found there to have a composition equivalent to two dimethyl phosphate anions plus a proton. For a plausible structure and a mechanistic sequence for its formation and subsequent disruption in the case of **2**, we suggest Scheme IV. In this scheme, we picture the ions of masses 349 and 251 as oxyphosphorane structures with pentacovalent phosphorus.

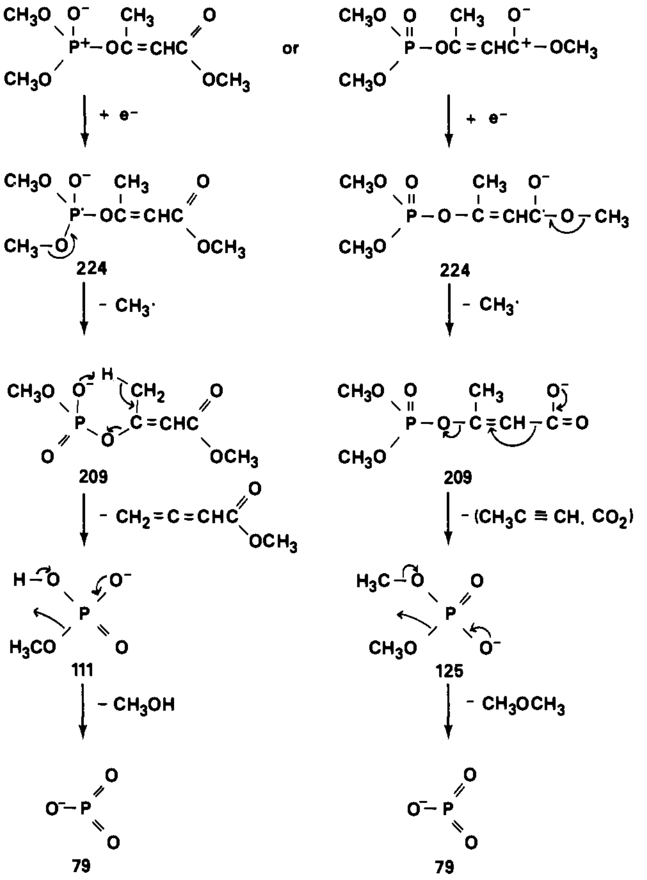
The analogous cluster ion formed in the first step shown, attachment of the dimethyl phosphate anion to an ester molecule, is observed in the NICI spectrum of **1** under higher than normal sample pressure (see Table I), where it probably arises by the same mechanism.

The second most frequent precursor of PO_3^-, as indicated by accelerating-voltage scans on the peak of mass 79 in the spectra of the five compounds, is the ion of mass 111, $(CH_3O)(HO)PO_2^-$. In the case of **2**, this parent/daughter relationship is confirmed by a CID-MIKE scan on the ion beam of mass 111, which shows three daughter ions, of mass and, in parentheses, relative intensity 110 (10), 96 (13), and 79 (100). Only the vinyl phosphate **2** shows the methyl phosphate anion in its NICI spectrum; in the other phosphates, it is apparently formed with enough excess energy that no detectable amount of it survives the required transit time through the instrument. Its principal demonstrated precursors in **1** and **2**, as shown by the appropriate CID-MIKE scans (see Tables IV and V), are most likely the $(M - CH_3)^-$ ions. We suspect that $(M - CH_3)^-$ is likewise an intermediate in the formation of $(CH_3O)(HO)PO_2^-$ in **3**–**5**. We visualize the reaction paths leading to $(CH_3O)(HO)PO_2^-$ and to the seemingly preferred (see Table V) product $(CH_3O)_2PO_2^-$ from $(M - CH_3)^-$ in **2** as shown in Scheme V. Similar reaction sequences can be written for **1**, **3**, **4**, and **5**. In the latter three compounds, the migrating hydrogen atom must come from the aryl ring.

Scheme IV

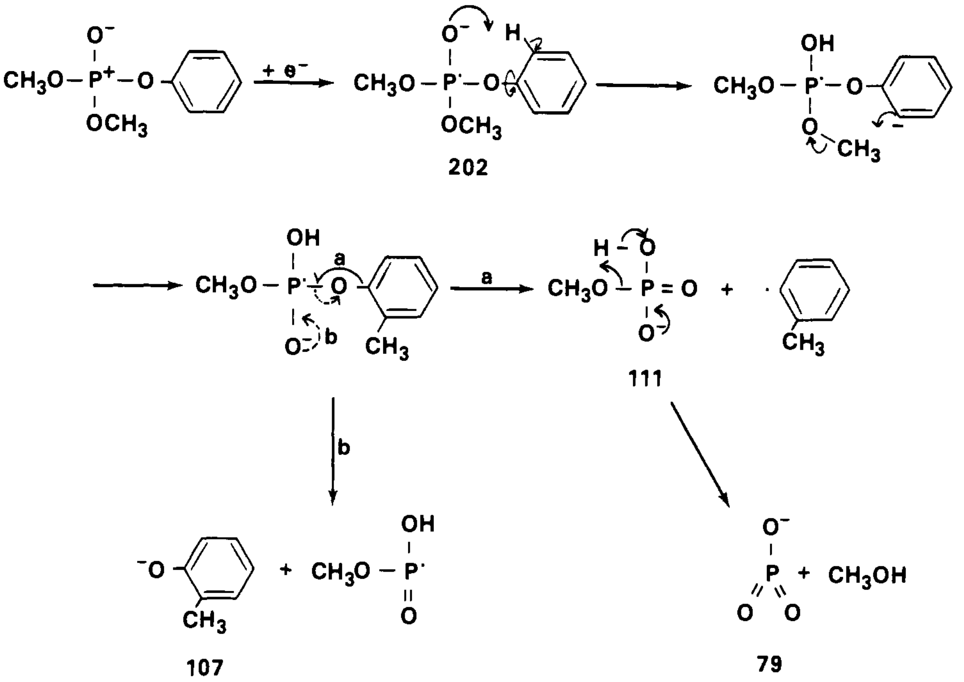


Scheme V



The $C_7H_7O^-$ ion observed in the NICI spectrum of **3** (see Table VII), as well as in the CID-MIKE spectrum of the corresponding $(M - CH_3)^-$ ion (see Table XI), contains the elements of the aryloxy group plus a methyl group less a hydrogen atom. Such an interaction between the aryl and methyl groups may also be incorporated in a sequence leading directly from the molecular radical anion to $(CH_3O)(HO)PO_2^-$ (Scheme VI), which may then react further as above to yield $CH_3OH + PO_3^-$.

Scheme VI



The dimethyl phosphate anion, $(CH_3O)_2PO_2^-$, which accounts for well over 90% of total ion yield in the NICI spectra of the vinyl phosphates **1** and **2**, is also prominent in those of the aryl phosphates but to a lesser extent. Moreover, its contribution, about 68% of total ion yield in the phenyl (**3**) and nitrophenyl (**4**) phosphate spectra, drops to 5% in that of the dinitrophenyl phosphate (**5**). The slack is taken up by aryloxy and aryl ions, which together comprise 14%, 16%, and 95% of total ion yield in the respective spectra. The trend, especially the large jump from mono- to dinitrophenyl, parallels the progessively increasing electron affinity and parent negative-ion lifetime in the sequence benzene < nitrobenzene < dinitrobenzene.[31]. Thus we view the drift in spectral features in terms of competition for the negative charge between the phosphate and aryl groups.

The three mass 79 precursors (Table X) unique to the dinitrophenyl phosphate **5** fall into place within this context. Beyond doubt, they give rise to the C_4HNO^- and $C_5H_3O^-$ ions that accompany PO_3^- in the spectrum of this phosphate (Table VI), although details are not entirely clear. The ions of masses 183 and 137 correspond to sequential loss of $(CH_3O)_2PO\cdot$ and $NO_2\cdot$ from the molecular radical anion (Table IX). That of mass 153, $C_6H_5N_2O_3^-$, appears unduly rich in hydrogen atoms and poor in oxygens. It most likely arises by loss of $(CH_3O)_2PO\cdot$ from the molecular radical anion of a compound in which one nitro group of **5** has been reduced to amino. Such inadvertent reduction in the mass spectrometer has been reported in a number of nitro compounds in both electron-impact[45] and CI[46] mass spectra. As a matter of passing interest, we note that the CID-MIKE scan of the mass 183 peak in the NICI spectrum of **5** (Table XIII) furnishes evidence for an isobaric species of mass 153, $C_6H_3NO_4^-$, arising by loss of NO· from the dinitrophenoxy ion via a nitro–nitrite rearrangement. Such a process, well-known in both positive- and negative-ion mass spectra of nitroarenes,[47] appears also in two other CID-MIKE scans, those of the mass 138 peak in the spectrum of **4** (Table XII) and of the mass 167 peak in the spectrum of **5** (Table XIII).

Summary

The negative-ion chemical-ionization mass spectra of the dimethyl vinyl and dimethyl aryl phosphates studied appear remarkably simple and straightforward. A large part of the total ion yield in every case consists of the dimethyl phosphate anion, $(CH_3O)_2PO_2^-$, which undergoes some further degradation spontaneously and more so upon collisional activation to yield PO_3^-, the monomeric metaphosphate anion. Our data reveal paths to PO_3^- formation from several additional precursors, most notably the monomethyl phosphate anion, $(CH_3O)(HO)PO_2^-$. Collision-induced dissociation of PO_3^- leads only to an oxygen atom and PO_2^-, the metaphosphite anion. The phenyl, nitrophenyl, and especially dinitrophenyl groups in the aryl phosphates appear to compete effectively with the phosphoryl group for the negative charge during anionic decomposition, in sharp contrast with the vinyl groups in the vinyl phosphates.

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Registry No. 1, 7786-34-7; **2**, 7786-34-7; **3**, 10113-28-7; **4**, 950-35-6; **5**, 66391-31-9; PO_3^-, 15389-19-2; PO_2^-, 20499-58-5; phenyl phosphorodichloridate, 770-12-7; 4-nitrophenol, 98-95-3; methyl phosphorodichloridate, 677-24-7; 2,4-dinitrophenyl phosphate, 2566-26-9; diazomethane, 334-88-3.

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(45) (a) Beynon, J. H.; Hopkinson, J. A.; Lester, G. R. *Int. J. Mass Spectrom. Ion Phys.* **1969**, *2*, 291. (b) Meyerson, S.; Vander Haar, R. W.; Fields, E. K. *J. Org. Chem.* **1972**, *37*, 4114. (c) Meyerson, S.; Fields, E. K. *Org. Mass Spectrom.* **1974**, *9*, 485.

(46) (a) Min, B. H.; Garland, W. A. *J. Chromatogr.* **1977**, *139*, 121. (b) Maquestiau, A.; Van Haverbeke, Y.; Flammang, R.; Mispreuve, H.; Elguero, J. *Org. Mass Spectrom.* **1979**, *14*, 117. (c) Brophy, J. J.; Diakiw, V.; Goldsack, R. J.; Nelson, D.; Shannon, J. S. *Org. Mass Spectrom.* **1979**, *14*, 201. (d) Harrison, A. G.; Kallury, R. K. M. R. *Org. Mass Spectrom.* **1980**, *15*, 284. (e) Yinon, J.; Laschever, M. *Org. Mass Spectrom.* **1981**, *16*, 264.

(47) Yinon, J. *Mass Spectrom. Rev.* **1982**, *1*, 257 and references cited there.