Fragmentation of Protonated O,O-Dimethyl O-Aryl Phosphorothionates in Tandem Mass Spectral Analysis

Tuula Kuivalainen

Department of Chemistry, Laboratory of Organic Chemistry, P. O. Box 55 (A. I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland

Risto Kostiainen

Environmental Laboratory of Helsinki, Helsinginkatu 24, 00530 Helsinki, Finland

Heikki Björk

The Finnish Research Project on the Verification of Chemical Disarmament, Department of Chemistry, P. O. Box 55 (A. I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland

Rolf Uggla and Markku R. Sundberg

Department of Chemistry, Laboratory of Inorganic Chemistry, P. O. Box 55 (A. I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland

A study was carried out on the fragmentation of 12 protonated O,O-dimethyl O-aryl phosphorothionates by tandem quadrupole mass spectrometry. Some of the studied compounds are used in agriculture as pesticides. Energy-resolved and pressure-resolved experiments were performed on the $[M + H]^+$ ions to investigate the dissociation behavior of the ions with various amounts of internal energy. On collisionally activated dissociation, the $[M + H]^+$ ions decompose to yield the $[M + H - CH_3OH]^+$, $(CH_3O)_2PS^+$ (m/z 125), and $(CH_3O)_2PO^+$ (m/z 109) ions as major fragments. The ions $[M + H - CH_3OH]^+$ and $(CH_3O)_2PS^+$ probably arise from the $[M + H]^+$ ions of the O,O-dimethyl O-aryl phosphorothionates with the proton on the sulfur or on the oxygen of the phenoxy group. The origin of the hydroxy proton of the methanol fragment was in many cases, surprisingly, the phenyl group and not the reagent gas. This was confirmed by using deuterated isobutane, C_4D_{10}, as reagent gas in CI. The fragment ions $(CH_3O)_2PO^+$ and $[ZPhS]^+$ are the results of thiono–thiolo rearrangement reaction. The precursor ion for the ion $(CH_3O)_2PO^+$ arises from most compounds upon chemical ionization, whereas the precursor ion for the ion $[ZPhS]^+$ arises only from a few compounds upon chemical ionization. The observed fragments imply that several sites carry the extra proton and that these sites get the proton usually upon ionization. The stability order and some characteristics of three protomers of O,O-dimethyl O-phenyl phosphorothionate were investigated by ab initio calculations at the RHF/3-21G* level of theory. (*J Am Soc Mass Spectrom 1995, 6, 488–497*)

Organophosphorus pesticides are widely used in modern agriculture. One important class of organophosphorus pesticides is the O,O-dialkyl O-aryl phosphorothionates, where a formally pentavalent phosphorus is bound to sulfur, two alkoxy groups, and one phenoxy group (Figure 1).

The O,O-dialkyl O-aryl phosphorothionates used as pesticides have been studied by mass spectrometry via a variety of ionization techniques [1, 2]. However, only a few publications that deal with collisionally acti-

vated dissociation tandem mass spectrometry (CAD-MS/MS) have appeared [3–6]. Hummel and Yost [3] presented the collisionally activated dissociation (CAD) spectra of the $[M + H]^+$ ions of some phosphates, phosphorodithioates, and phosphorothionates produced by using triple stage quadrupole mass spectrometer and methane as the reagent gas. The fragment ions of m/z 125 $[(CH_3O)_2PS^+]$ and m/z 109 $[(CH_3O)_2PO^+]$ were seen in most of the CAD spectra of the protonated O,O-dimethyl phosphorothionates studied. The $[M + H]^+$ ions of all protonated O,O-dimethyl phosphorothionates showed a neutral loss of 32 u (CH_3OH). Roach and Andrzejewski [4] published a tandem mass spectrometry study on some phos-

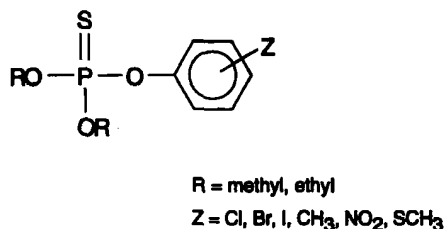R = methyl, ethyl

Z = Cl, Br, I, CH$_3$, NO$_2$, SCH$_3$

Figure 1. Structure of O,O-dialkyl O-aryl phosphorothionates.

phates, phosphorodithioates, phosphorothiolates, and phosphorothionates. Electron-ionization (EI), CAD mass-analyzed, mass-analyzed ion kinetic energy experiments were performed in a reversed-geometry douple-focusing magnetic sector instrument. EI and methane chemical ionization (CI) CAD-MS/MS experiments were performed on a triple-quadrupole instrument. The ions that correspond to [ZPhS]$^+$ in the daughter spectra of the [M + H]$^+$ ions of some O,O-dimethyl O-aryl phosphorothionates suggested aryl migration to sulfur. Kenttämaa and co-workers [6] used multiple stage mass spectrometry (MS^3) to examine the structures of some low mass fragment ions commonly produced upon collisional activation of the molecular ions of O,O-dialkyl O-aryl phosphorothionates. The experiments were carried out on a Fourier transform ion cyclotron resonance mass spectrometer. The findings showed, for example, that the fragment ion of m/z 125 formed from the molecular ion of O,O-dimethyl O-4-chlorophenyl phosphorothionate is the result of a complex rearrangement that involves transfer of an alkylene group to the aromatic ring from the phosphorus-containing part of the molecular ion. The mass value of the product ion is therefore dependent on the substituents of the aromatic ring as well as on the phosphorus-containing part of the precursor molecule. The fragment ion of m/z 125 generated from the molecular ion of O,O-dimethyl O-4-chlorophenyl phosphorothionate is different from that obtained from protonated O,O-dimethyl O-2-chlorophenyl and O,O-dimethyl O-(2,4-dichlorophenyl) phosphorothionates.

CI CAD-MS/MS in combination with gas chromatography (GC) offers a fast and selective method for reliable identification of pesticides, especially when the sample is a complex mixture and may contain more than one isomer. However, the fragmentation reactions caused by collisional activation are not yet well established. We describe here a study of the collision-induced fragmentation reactions of 12 O,O-dimethyl O-aryl phosphorothionates protonated by isobutane CI. The CAD-MS/MS daughter spectra of [M + H]$^+$ ions of several of the compounds studied have not been discussed before. Our unique series includes different isomers that allow a detailed discussion of fragmentation in a tandem quadrupole mass spectrometer. Six of the compounds were commercial pesticides; the others were of interest as potential pesticides or as substances that enhance the activity of known insecticides. The

energy- and pressure-resolved CAD experiments were performed on the protonated compounds to get more detailed insight into their dissociation behavior. In addition, deuterated isobutane as the reagent gas in chemical ionization was used to confirm the proposed fragmentation pathways. Finally, ab initio quantum-mechanical calculations were carried out to characterize the structures of three protomers of O,O-dimethyl O-phenyl phosphorothionate. The stability order of these three protomers was predicted on the basis of these theoretical calculations.

Experimental

Chemicals

The structures of the O,O-dimethyl O-aryl phosphorothionates studied, together with their chemical names, common names, molecular weights, and numbers that are used to refer to them, are listed in Table 1. The commercial organophosphorus pesticides fenchlorphos, bromophos, iodofenphos, methyl parathion, fenitrothion, and fenthion were obtained from the State Institute of Agricultural Chemistry (Finland). Compounds 1 [7, 8], 2 [9, 10], 3 [9, 10], 4 [7, 11], and 6 [9, 10] were synthesized by methods described earlier. Compound 5 was prepared by the method described for 4 [7, 11]. Compounds 1, 3, and 4 were purified by distillation. The purity of all the compounds was confirmed by GC and NMR. The proton noise decoupled ^{31}P − {^{1}H} NMR spectra for O,O-dimethyl O-aryl phosphorothionates were recorded at 40 MHz. The ^{31}P chemical shifts distributed between 65.56 and 66.78 ppm [relative to the external standard P(OH)$_4^+$ClO$_4^-$ in D$_2$O]. Isobutane (Aga Co., Germany; purity 99.95%) and deuterated isobutane C$_4$D$_{10}$ (Cambridge Isotope Laboratories, Inc., Woburn, Ma; 99% deuterium) were used as the reagent gases. Argon (Aga Co., purity 99.998%) was used as the collision gas for the CAD experiments.

Instrumentation

All the mass spectrometry experiments were carried out with a Finnigan-MAT (San Jose, CA) triple stage quadrupole (TSQ) 45 A mass spectrometer equipped with an Incos data system. Isobutane at a pressure of 0.6 torr provided the reagent gas for chemical ionization. Some experiments also were carried out by using deuterated isobutane C$_4$D$_{10}$ as the reagent gas. The temperature of the ion source was 120 °C. The electron energy was 150 eV and the emission current was 0.3 mA. The mass spectrometer was operated in the daughter ion scan mode. The CAD measurements were carried out with a collision gas (argon) pressure of 0.8 mtorr and a collision energy of 20 eV (E_{lab}). The energy-resolved experiments were performed on the protonated compounds 1–12 by recording successive daughter spectra as the collision energy was increased

Table 1. Names, molecular weights (monoisotopic), and structures of the O,O-dimethyl O-aryl phosphorothionates studied

Chemical name; common name	MW	Compound number	Structure
O,O-dimethyl O-phenyl phosphoro-thionate	218	1	
O,O-dimethyl O-2-chlorophenyl phosphorothionate	252	2	
O,O-dimethyl O-4-chlorophenyl phosphorothionate	252	3	
O,O-dimethyl O-(2,4-dichloro-phenyl) phosphorothionate	286	4	
O,O-dimethyl O-(2,5-dichloro-phenyl) phosphorothionate	286	5	
O,O-dimethyl O-(3,4-dichloro-phenyl) phosphorothionate	286	6	
O,O-dimethyl O-(2,4,5-trichloro-phenyl) phosphorothionate; fenchlorphos	320	7	
O,O-dimethyl O-(4-bromo-2,5-dichlorophenyl) phosphorothionate; bromophos	364	8	
O,O-dimethyl O-(2,5-dichloro-4-iodophenyl) phosphorothionate; iodofenphos	412	9	
O,O-dimethyl O-4-nitrophenyl phosphorothionate; methyl parathion	263	10	
O,O-dimethyl O-(3-methyl-4-nitro-phenyl) phosphorothionate; fenitrothion	277	11	
O,O-dimethyl O-[3-methyl-4-(methyl-thio)phenyl] phosphorothionate; fenthion	278	12	

in ~ 5-eV intervals from 5 up to 30 eV (E_{lab}), at a collision gas pressure of 0.8 mtorr. The pressure-resolved experiments were performed on the [M + H]$^+$ ions of compounds 1, 2, 3, 5, 7, 8, 9, and 12 at collision gas pressure of 0.1, 0.4, 0.6, and 0.8 mtorr, at a collision energy of 20 eV. Collision gas pressure of 0.1 mtorr probably corresponds to single collision conditions [12] and that of 0.8 mtorr corresponds to multiple collision conditions. In 20-eV CAD experiments and pressure-resolved experiments, the samples were introduced through a Finnigan-MAT 9611 gas chromatograph interfaced by direct coupling to the mass spectrometer. A silica capillary column SE-54 (HNU-Nordion, Finland; 25 m, 0.32 mm, 0.25 μm), an injector temperature of 220 °C, and helium carrier gas at a flow rate of about 1.5 mL min^{-1} was used. A temperature program started at 60 °C (1 min), with a final temperature of 250 °C (15 °C min^{-1}), was used. The interface temperature was 260 °C. In energy-resolved experiments the samples were introduced by direct inlet (direct exposure probe, Finnigan-MAT) by heating the filament with the current. The heating rate was 2 mA s^{-1}. The breakdown graphs were constructed based on peak intensities normalized to the total fragment ion current at each collision energy and each collision gas pressure.

Ab initio calculations were carried out by the Gaussian 92 program [13] on Convex 3840 (Convex Corporation, Dallas, TX) and Cray X-MP-Unicos (Cray Research Inc., Chippewa Falls, WI) computers at the Center of Scientific Computing of Finland. Geometry optimizations were performed by analytical gradient-based techniques at the RHF/3-21G* level of theory. The RHF/3-21G* vibrational frequences were computed for each optimized species to characterize them as true minima. No imaginary frequences were found. Natural bond orbital (NBO) analyses were performed for each species to evaluate the electronic properties [14].

Results and Discussion

The ions [M + H]$^+$ were produced with isobutane CI, the plasma of which, at 0.6 torr, contains tert-butyl cation [t-C$_4$H$_9$]$^+$ (97% relative abundance) and isopropyl cation [C$_3$H$_7$]$^+$ (3%). The proton affinity of isobutene (the conjugate base of the Brönsted acid [t-C$_4$H$_9$]$^+$) is 819.6 kJ mol^{-1} and that of propene (the conjugate base of the Brönsted acid [C$_3$H$_7$]$^+$) is 751.0 kJ mol^{-1} [15]. Under isobutane CI conditions, the phosphorothionates studied form intense [M + H]$^+$ ions with little fragmentation, which indicates that the proton affinities of the phosphorothionates are close to the PA of isobutene and a small amount of energy is transferred in protonation reactions. The CI spectra also were recorded for compounds 1, 2, 3, and 12 by using deuterated isobutane C$_4$D$_{10}$ as the reagent gas. Inspection of the isotopic patterns of [M + H]$^+$ and [M + D]$^+$ ions in the C$_4$H$_{10}$ and C$_4$D$_{10}$ CI spectra revealed that no proton–deuteron exchange occurs un-

der deuterated isobutane CI conditions. To get more detailed information about the fragmentation pathways the CAD spectra also were recorded for compounds 1, 3, 4, 6, 10, 11, and 12 by using deuterated isobutane C$_4$D$_{10}$ as the reagent gas in chemical ionization.

The initial protonation produces [M + H]$^+$ ions with an excess internal energy. These excited ions [M + H]$^{+*}$ are assumed to be sufficiently long lived that the excess energy is randomized among the internal degrees of freedom. Upon collision with the plasma, the [M + H]$^{+*}$ ions may undergo collisional stabilization, which produces a collection of [M + H]$^+$ ions [15], where the proton may be attached on different basic sites of molecules. The conceivable protonation sites of the compounds studied here are the oxygens, the sulfur, the benzene ring, and the substituents on the benzene ring. The proton affinities of trimethylphosphorothionate (CH$_3$O)$_3$PS, benzene, chlorobenzene, and nitrobenzene are 897.5, 758.6, 760.2, and 809.2 kJ mol^{-1}, respectively [16]. Accordingly, protonation of O,O-dimethyl O-phenyl, O,O-dimethyl O-chlorophenyl, and O,O-dimethyl O-nitrophenyl phosphorothionates can be expected to occur predominantly on the phosphorothionate moiety when isobutane is used as the reagent gas in CI.

Ab Initio Calculations

To investigate the stability order of different protomers we carried out ab initio quantum-mechanical calculations for three protomers of compound 1 (a, b, c). Protomer a has a proton on the sulfur, protomer b has a proton on the oxygen of the phenoxy group, and protomer c has a proton on the methoxy group. The calculations were performed at 3-21G* (including the d-orbital-like functions) level. Figure 2 shows the optimized geometries of protomers a, b, and c. Each structure represents the energy minimum. The calculated bond lengths (angstroms) and ab initio energies E(RHF) are given in Figure 3. The present ab initio calculations suggest that for protonated 1, the most stable protomer is a. Protomer a is 73.7 kJ mol^{-1} and protomer b is 2.1 kJ mol^{-1} more stable than protomer c (1 a.u. corresponds to 2625.4 kJ mol^{-1}). Accordingly, the thermodynamically preferred protonation site is the sulfur. NBO analyses were performed on protomers a, b, and c. According to natural population analysis there is a remarkable excess of electrons in the oxygens (natural charge −0.791 to −0.917), whereas the phosphorus bears high positive charge (natural charge +2.183 to +2.426). This situation can be interpreted by strong polarization of the P—O bonds. Consequently, the protomer a can be regarded as an electron pair donor–electron pair acceptor complex, where three ions are coordinated to the +P—S—H group. The protomers b and c can be regarded as electron pair donor–electron pair acceptor complexes, where two ions and one neutral molecule are coordi-
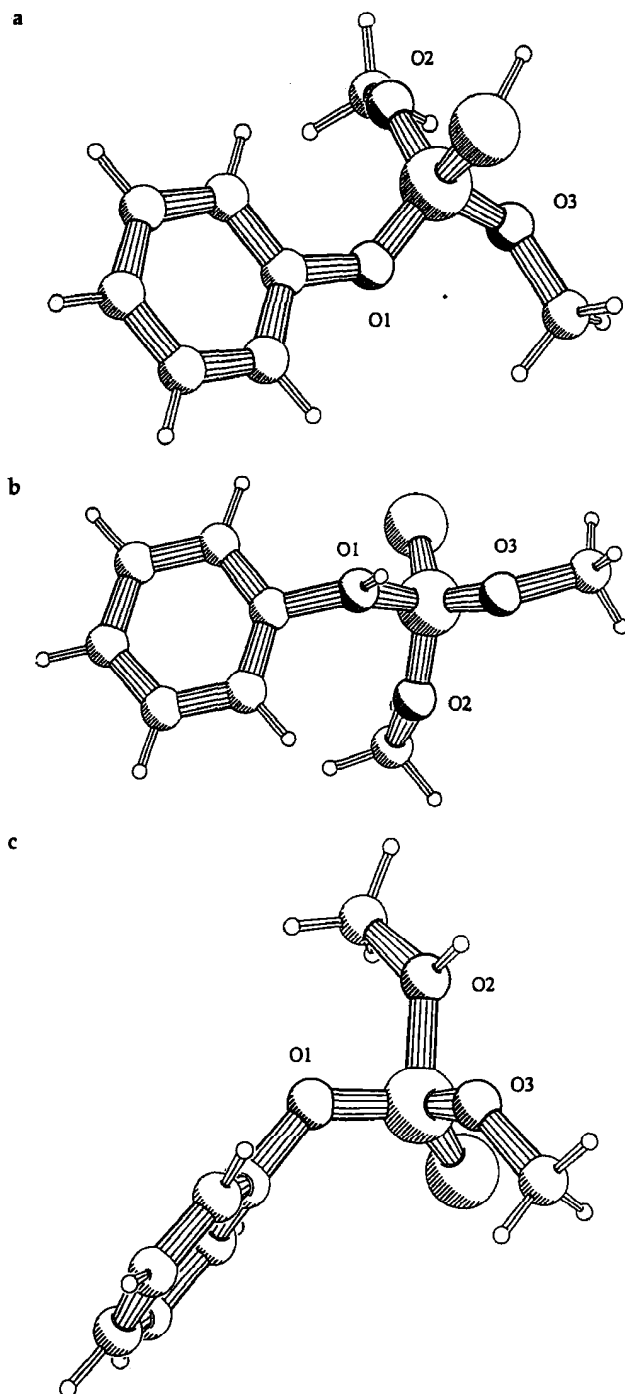
a

b

c

Figure 2. 3-21G*-optimized geometries for protomers a, b, and c of O,O-dimethyl O-phenyl phosphorothionate (1).

a

E(RHF)= - 1266.228062 a.u.

b

E(RHF)= - 1266.199989 a.u.

c

E(RHF)= - 1266.199191 a.u.

Figure 3. Computed bond lengths (angstroms) and E(RHF) energies (atomic units) for protomers a, b, and c of compound 1.

nated to the $+P$—S^- group. The calculated stabilizing donor–acceptor interaction energies between oxygen lone pairs and lp^*-orbitals of phosphorus are presented in Table 2.

Fragmentation of the $[M + H]^+$ Ions

Table 3 summarizes the 20-eV CAD-MS/MS daughter ion spectra obtained for the $[M + H]^+$ ions of the O,O-dimethyl O-aryl phosphorothionates. The parameters commonly varied in the TSQ mass spectrometer

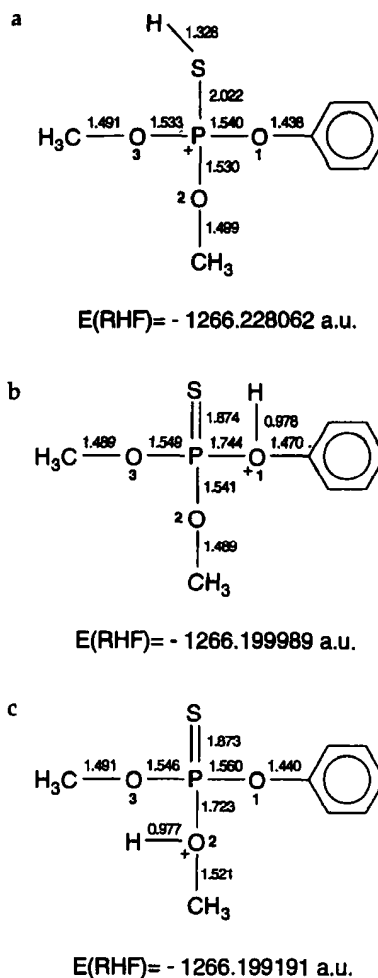to vary energy deposition on the parent ion are collision energy and collision gas pressure (the number of activation steps). Figure 4 shows the energy-resolved curves for the compounds 1, 2, 3, 11, and 12. Figure 5 shows the pressure-resolved curves for 1, 2, 3, and 12.

The most abundant fragment ions in the 20-eV CAD spectra were $(CH_3O)_2PS^+$ (m/z 125), $[M + H - CH_3OH]^+$, and $(CH_3O)_2PO^+$ (m/z 109) (Table 3). The ion $(CH_3O)_2PS^+$ probably arises from molecules with the proton on the oxygen of the phenoxy group (protomer b) [Scheme I(i)]. Comparison of the calculated electron donor–acceptor interaction energies between the oxygens and the phosphorus for the protomer b of compound 1 (Table 2) showed that the P—O(1) bond is remarkably weaker than the other two P—O bonds.

Table 2. The sums for the electron donor–acceptor interaction energies[a] (kJ mol^{-1}) between oxygen lone pairs and lp^*-orbitals of phosphorus for protomers a, b, and c of compound 1 with the 3-21G* basis set

	P—O(1)	P—O(2)	P—O(3)
a	2564.4	2710.0	2720.9
b	1279.5	2672.7	2695.3
c	2349.7	930.5	1654.4

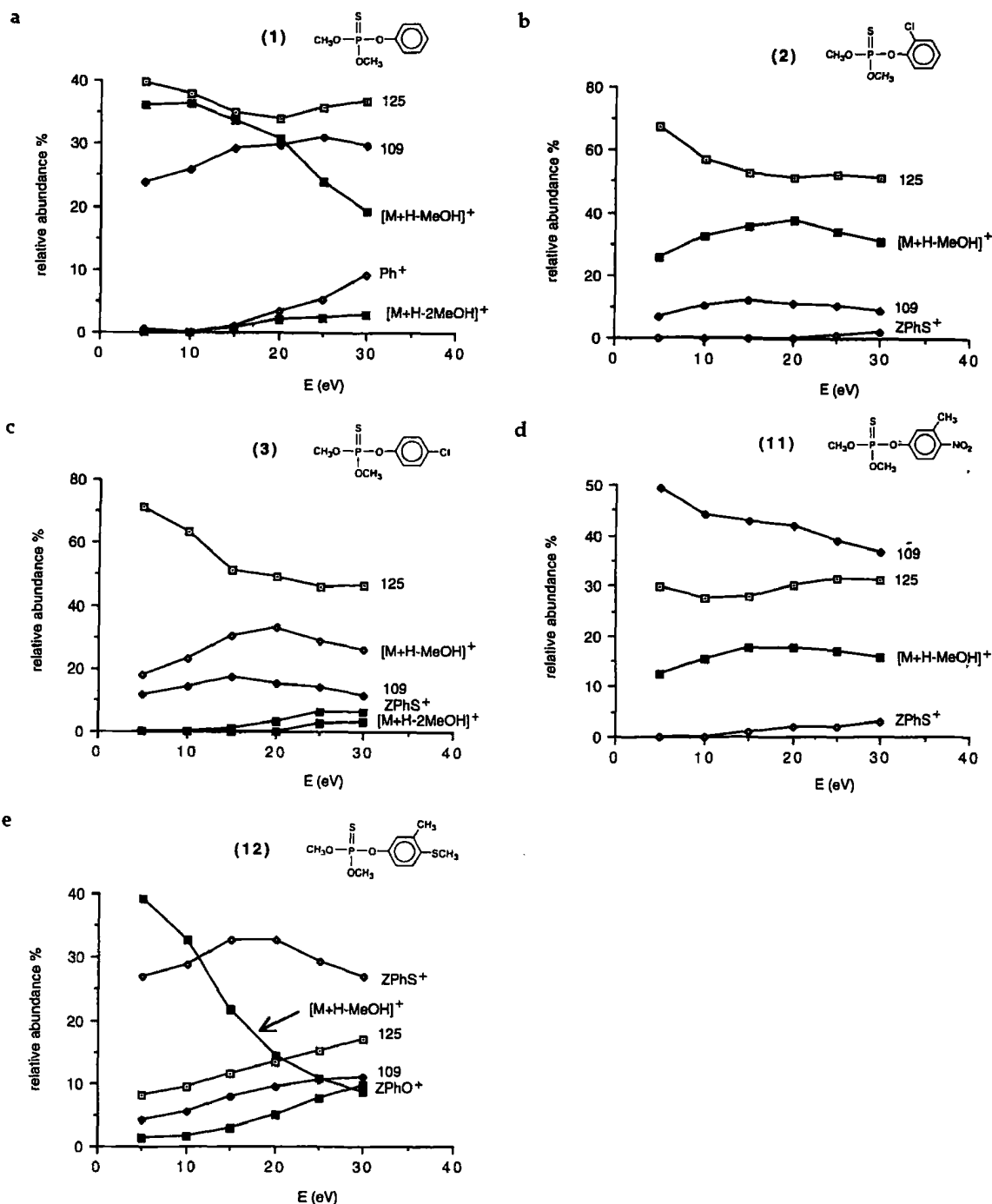[a] $E(2)$ in NBO notation.

Figure 4. Energy-resolved curves of the [M + H]$^+$ ions of O,O-dimethyl O-aryl phosphorothionates: (a) **1**; (b) **2**; (c) **3**; (d) **11**; (e) **12**. The total ion current was calculated by excluding the parent ion. The curve "109" of compound **1** represents the behavior of two ions; (CH$_3$O)$_3$PO$^+$ and PhS$^+$.

In addition, the P—O(1) distance in **b** is substantially longer than the other two P—O distances (Figure 3). These ab initio results may offer an explanation for the favorable neutral loss of phenol from **b** under energetic conditions created by collision activation. The fragment ion (CH$_3$O)$_2$PS$^+$ dominates the daughter patterns of compound **1** and its halogenated derivatives **2**—**9** at the collision energies used (Table 3, Figure 4).

The ions [M + H − CH$_3$OH]$^+$ were at first expected to arise from molecules with the proton on the

oxygen of a methoxy group. However, the use of deuterated isobutane as the reagent gas in chemical ionization changed this assumption. The 20-eV CAD spectra of the [M + D]$^+$ ions of the compounds **1, 3, 6, 10, 11,** and **12** exhibited surprisingly the fragment ions [M + D − CH$_3$OH]$^+$ instead of the fragment ions [M + D − CH$_3$OD]$^+$; compound **4** produced approximately equal amounts of ions [M + D − CH$_3$OH]$^+$ and [M + D − CH$_3$OD]$^+$. If the initial protonation had occurred on the ring, there should be an equal probability of losing CH$_3$OH and CH$_3$OD from the [M +
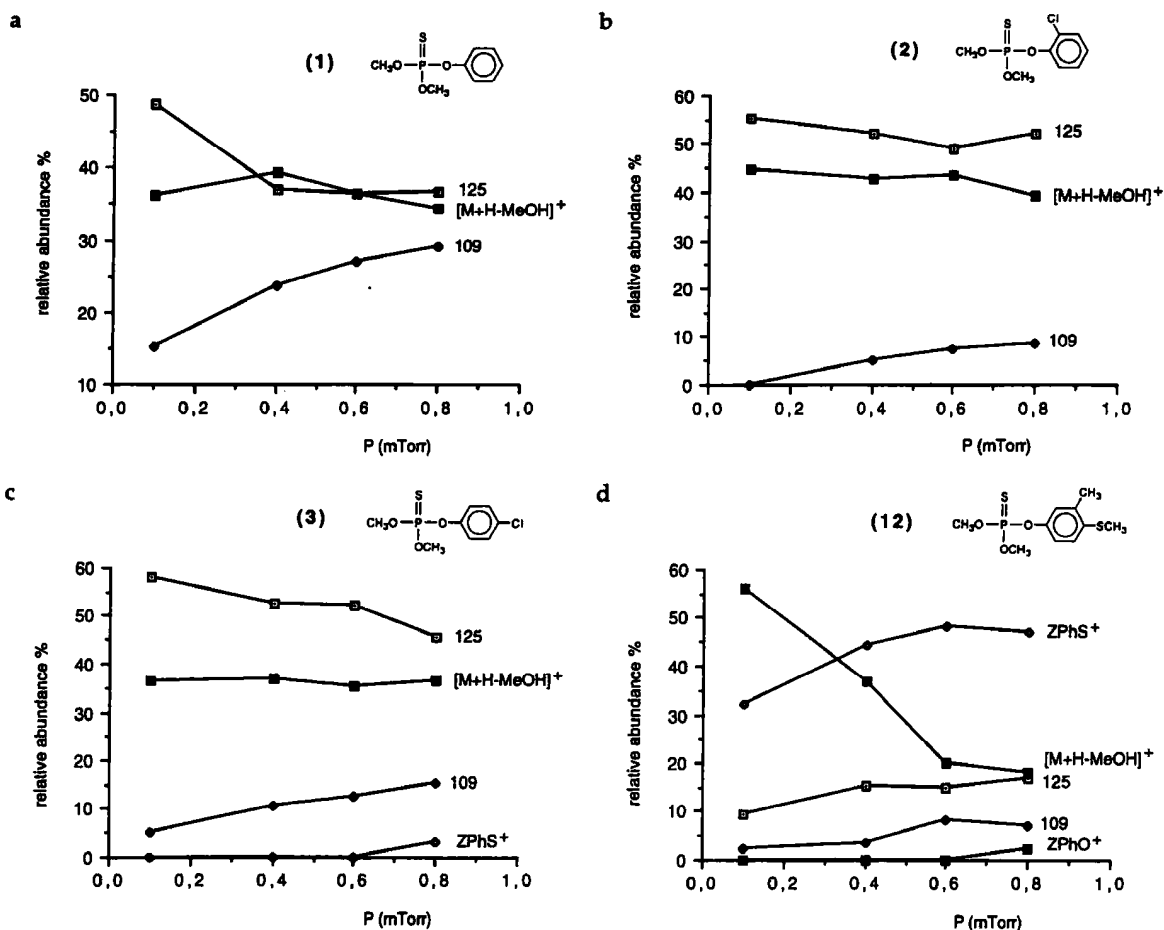
Figure 5. Pressure-resolved curves of the $[M + H]^+$ ions of O,O-dimethyl O-aryl phosphorothionates: (a) 1; (b) 2; (c) 3; (d) 12. The total ion current was calculated by excluding the parent ion. The curve "109" of compound 1 represents the behavior of two ions: $(CH_3O)_3PO^+$ and PhS^+.

Table 3. CAD-MS/MS spectra of ions $[M + H]^+$ of O,O-dimethyl O-aryl phosphorothionates

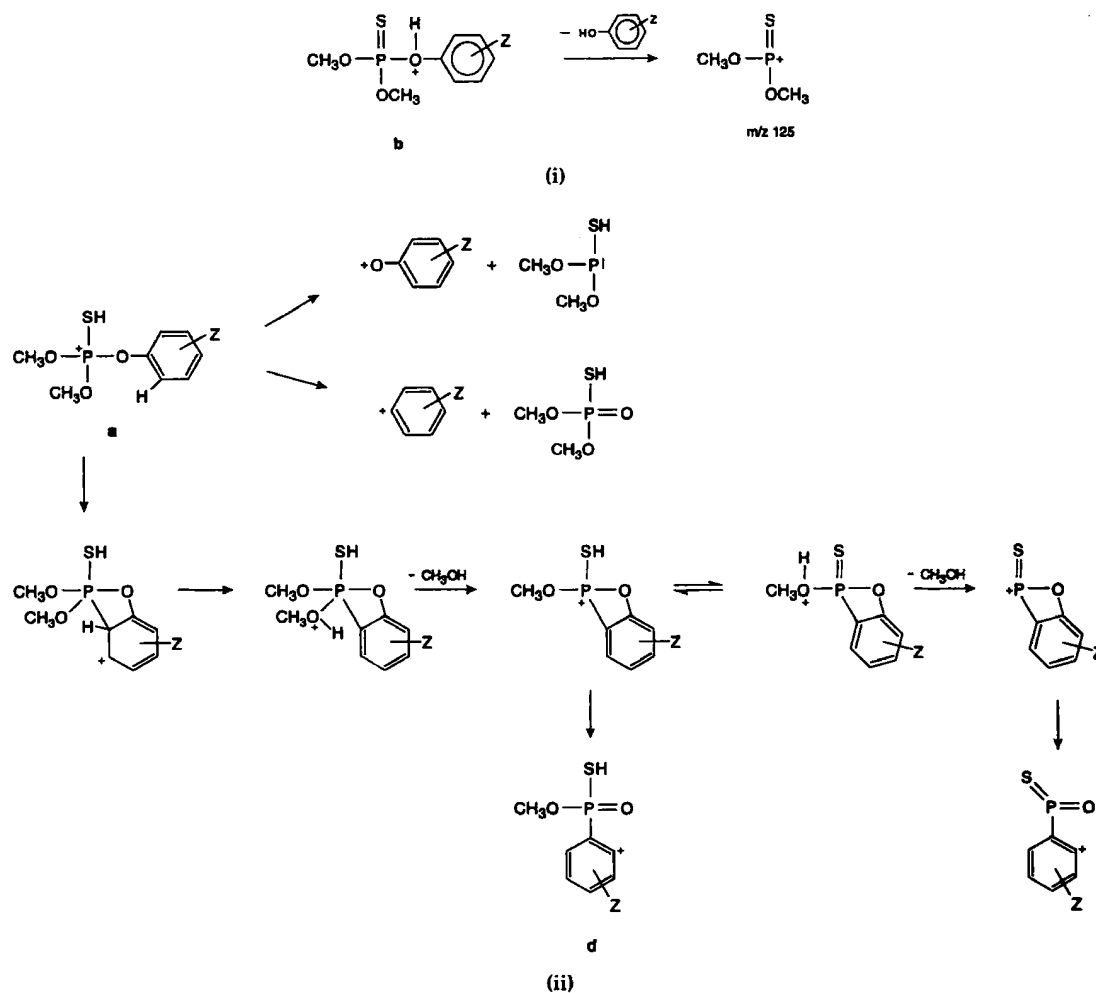|				Ion m/z (relative abundance)[a]					
Compound	$[M + H]^+$	$(CH_3O)_2PS^+$ m/z 125	$(CH_3O)_2PO^+$ m/z 109	$[M + H - CH_3OH]^+$	$[ZPhS]^+$	$[ZPhO]^+$	$[M + H - 2CH_3OH]^+$	$[ZPh]^+$	Other ions
1	219(100)	79	62[b]	187(56)	109(16)[b]	—	155(5)	77(8)	—
2	253(100)	89	24	221(74)	143(5)	127(2)	189(2)	111(2)	206(4)
3	253(85)	100	39	221(59)	143(13)	127(4)	189(9)	111(4)	—
4	287(76)	100	16	255(61)	177(2)	161(14)	223(1)	—	240(1)
5	287(90)	100	36	255(67)	177(3)	161(1)	223(2)	—	240(4)
6	287(100)	82	50	255(49)	177(12)	161(2)	223(9)	145(2)	—
7	321(93)	100	25	289(58)	211(2)	195(7)	—	—	274(2)
8	365(75)	100	29	333(33)	—	239(3)	—	—	—
9	413(100)	86	28	381(30)	303(1)	287(3)	—	—	251(7)
10	264(100)	47	42	232(52)	154(2)	138(1)	200(1)	122(1)	123(4), 139(3), 186(2), 218(2)
11	278(100)	45	59	246(35)	168(3)	152(2)	214(1)	136(2)	93(2), 124(2), 137(2), 153(3), 200(3), 218(2)
12	279(82)	40	30	247(37)	169(100)	153(11)	—	137(4)	105(21), 138(24), 187(2), 232(4)

[a] Only relative abundances ≥ 1% are reported.
[b] The sum of the %RA of the ions $(CH_3O)_2PO^+$ and $[PhS]^+$ is 78%; the estimated %RA of $(CH_3O)_2PO^+$ and $[PhS]^+$ are 62% and 16%, respectively (see text).

D]$^+$ ion. Accordingly, this could be true for compound 4. However, our experimental results for the compounds 1, 3, 6, 10, 11, and 12 are not in accordance with this explanation. Formation of the ions [M + D − CH$_3$OH]$^+$ strongly suggests that the origin of the hydroxy proton of the methanol fragment in the spectra of the compounds 1, 3, 6, 10, 11, and 12 is the phenyl group. The proposed fragmentation is presented in Scheme I(ii). The neutral loss of methanol from the collisionally activated [M + H]$^+$ ions probably involves an intramolecular electrophilic aromatic substitution reaction in which the attacking electrophile is the positively charged phosphorus. The reaction may proceed through a four-center intermediate analogous to oxaphosphetane in the Wittig reaction. Our assumption is, however, that this kind of intermediate is unstable and isomerization to a more stable ion d may occur. The driving force for this state is presumably ring opening and the formation of a very strong P=O bond. Generally, aryl cations are not stable ions because the conjugation of the positive charge with the benzene ring is prevented as the empty

sp^2-orbital is directed orthogonally to the π-system. However, in the case of ion d, the stability may be influenced by the possibility to donate electron density through space from the oxygen of the phosphoryl group to the positive carbon. This kind of stabilization is enabled by the polarized P=O bond with electron density strongly skewed toward oxygen. The proposed mechanism for the loss of methanol from protomer a of compound 1 is supported by the following ab initio results: (1) comparison of the calculated electron donor-acceptor interaction energies between the oxygens and the phosphorus (Table 2) showed that the strengths of P—O bonds do not differ greatly from each other; (2) neither do the P—O distances differ markedly from each other (Figure 3); (3) the computed distance between phosphorus and C(2) of the benzene ring is 3.273 Å, but this does not exclude the possibility for the phosphorus to attack on C(2) of the benzene ring. These ab initio results also may give an explanation for the unfavorable loss of the ion PhO$^+$ from protonated 1 (protomer a). A minor fragment ion [ZPhO]$^+$ was observed, however, in the 20-eV spectra

(i)

(ii)

Scheme I

of the other protonated compounds 2–12. The energy-resolved curves (Figure 4) show that the loss of methanol from [M + H]$^+$ of the compounds 2, 3, and 11 is only slightly dependent on the exitation energy, whereas %RA (relative abundance) of the ions [M + H − CH_3OH]$^+$ of the compounds 1 and 12 decreases considerably when the collision energy is increased. Hence, at higher excitation energies there is a decreasing tendency for the loss of methanol from a protomer without any substituent or with an electron donating substituent on the benzene ring as a result of other competing fragmentation reactions (e.g., loss of two methanol molecules, loss of phenyl ion). A fragment ion [M + H − $2CH_3OH$]$^+$ appears in eight out of twelve 20-eV CAD spectra, with an intensity of 1–9%. However, this fragment ion was not observed at all in the 5–10-eV CAD spectra which indicates that the ion [M + H − CH_3OH]$^+$ does not have enough internal energy to fragment further.

Phosphorothionate esters have been reported to undergo thiono–thiolo rearrangement upon electron impact. Rearrangement takes place by aryl migration to sulfur [1, 17]:

O,O-dialkyl O-aryl phosphorothionate

O,O-dialkyl S-aryl phosphorothiolate
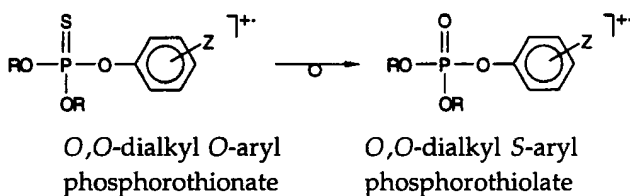
Neutral phosphorothionate esters have been reported to isomerize intermolecularly at high temperatures to produce thiono–thiolo rearrangement products by alkyl migration to sulfur. An O-methyl group is transferred much more readily than ethyl and higher alkyl groups. Aryl groups do not migrate at all [18]. Possible places for thermal isomerization in the experiments discussed here include the injector, column, interface, and ion source. However, the results suggest that no methyl migration occurs for the compounds studied.

The presence of the fragment ions $(CH_3O)_2PO^+$ (m/z 109) and [SPhZ]$^+$ in the CI CAD-MS/MS spectra of O,O-dimethyl O-aryl phosphorothionates suggests that a thiono–thiolo rearrangement reaction by aryl migration to sulfur occurs in our experimental conditions. The ion $(CH_3O)_2PO^+$ is likely to be produced by neutral loss of thiophenol HSPhZ from the isomerized ions [M + H]$^+$: O,O-dimethyl S-aryl phosphorothiolates protonated on the sulfur of the thiophenoxy group (e). The ion [SPhZ]$^+$ probably arises from the isomerized structures with the proton on the oxygen of the P=O group (f). The main fragmentation schemes proposed for the isomerized structures, protonated O,O-dimethyl S-aryl phosphorothiolates, are presented in Scheme II.

The energy-resolved curves (Figure 4) reveal that the ion of m/z 109 can be observed also at lower collision energies. Moreover, the amount of collision
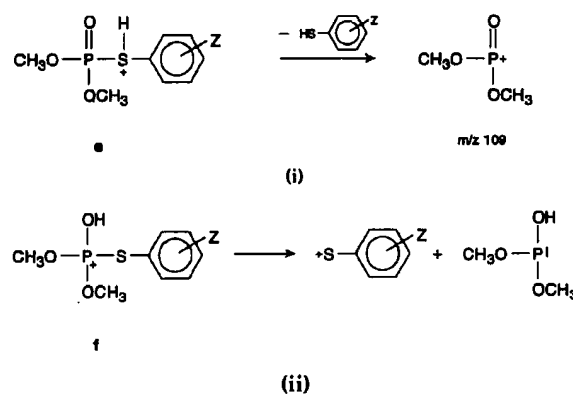
Scheme II

energy has no significant effect on the %RA of the ion of m/z 109, which either decreases slightly, increases slightly, or remains almost constant when the collision energy is raised. This suggests that the thiono–thiolo rearrangement occurs mainly in the ionization chamber. In the case of the studied compounds, the internal energy obtained upon chemical ionization may be high enough to allow unimolecular rearrangement to isomeric species, which results in formation of a collection of rearranged and unarranged [M + H]$^+$ ions. This hypothesis is supported also by the pressure-resolved CAD experiments: the spectra of all other compounds except 2 also exhibited the m/z 109 ion at lower collision gas pressures (Figure 5). When the collision gas pressure was increased so that multiple activation collisions occurred, the %RA of m/z 109 was either increased slightly or remained approximately constant. In Figures 4a and 5a, the curve "109" represents the behavior of the sum of two ions; $(CH_3O)_2PO^+$ and [PhS]$^+$.

The ion [ZPhS]$^+$, which probably arises from the ion f by cleavage of the phosphorus–sulfur bond [Scheme II(ii)], is the most abundant ion in the 20-eV spectrum of the compound 12 (Table 3). The ion [ZPhS]$^+$ is abundant also at lower collision energies (Figure 5d) and collision gas pressures (Figure 4e), which suggests that the ion f of the compound 12 is formed in the ionization chamber. Moreover, the ion [ZPhS]$^+$ dominates the dissociation patterns at higher collision energies as well as at higher collision gas pressures. The driving force for this favorable fragmentation pathway is the formation of the ion [ZPhS]$^+$ stabilized by the electron-donating resonance effect of the p-SCH_3 substituent. The abundance of the ion [ZPhS]$^+$ is especially low for the compounds with chloro substituent at C-2 on the benzene ring, probably because the ion [ZPhS]$^+$ is destabilized by electron-attracting chloro substituent at C-2. The energy-resolved curves (Figure 4c, d) show that at low collision energies, the fragmentation to yield the ion [ZPhS]$^+$ is not observed at all from [M + H]$^+$ ions of 3 and 11, and at

higher collision energies, the %RA of the ion [ZPhS]$^+$ is then quite low. The pressure-resolved curve (Figure 5c) shows that the ion [ZPhS]$^+$ from [M + H]$^+$ ions of 3 is observed only at higher collision gas pressures. When deuterated isobutane was used as the reagent gas the 20-eV CAD spectra of the compounds 3, 6, and 12 exhibited fragment ions [ZPhS + 1]$^+$ instead of ions [ZPhS]$^+$, which suggests that a proton–deuteron exchange reaction occurred. However, this kind of exchange reaction was not observed for compound 1.

The ion of m/z 109 in the spectrum of compound 1 can be either $(CH_3O)_2PO^+$ or PhS^+. To resolve which of the ions is in question, the ion [M + H + 2]$^+$ that contains isotopic sulfur atom ^{34}S was selected as the parent ion in the 20-eV CAD experiment. The spectrum exhibited the fragment ions of m/z 109 and 111. This indicates that m/z 109 is partly $(CH_3O)_2PO^+$ and partly PhS^+. The abundance of the latter ion is about one fourth of the former.

Conclusions

The aim of this study was to investigate the fragmentation behavior of the collisionally activated [M + H]$^+$ ions of 12 O,O-dimethyl O-aryl phosphorothionates. Perhaps the most surprising result obtained was that the origin of the hydroxy proton in the methanol fragment is usually not the reagent gas, isobutane, but unexpectedly the phenyl group of phosphorothionates. This was confirmed by using deuterated isobutane (C_4D_{10}) as the reagent gas in chemical ionization. The observed fragmentation upon CAD at several different collision energies and collision gas pressures implies that chemical ionization of O,O-dimethyl O-aryl phosphorothionates produces a collection of unrearranged and rearranged [M + H]$^+$ ions with the extra proton at several sites of the ion: unrearranged [M + H]$^+$ ions carried the proton on the sulfur (ion a) and on the oxygen of the phenoxy group (ion b); rearranged [M + H]$^+$ ions carried the proton on the sulfur of the thiophenoxy group (ion e) and on the oxygen of the P=O group (ion f). The CAD results suggest that the majority of the population of the fragmenting [M + H]$^+$ ions of compounds 1–9 consists of the phenoxy-O protonated ions (protomer b), although according to ab initio calculations for three protomers of compound 1, the thermodynamically preferred protonation site is sulfur.

Acknowledgments

References

1. Jörg, J.; Houriet, R.; Spiteller, G. Monatsh. Chem. 1966, 97, 1064–1087.
2. See, for example: (a) Damico, J. N. J. Assoc. Off. Anal. Chem. 1966, 49, 1027–1045; (b) Lovins, R. E. J. Agric. Food Chem. 1969, 17, 663–667; (c) Rankin, P. C. J. Assoc. Off. Anal. Chem. 1971, 54, 1340–1348; (d) Bohn, G.; Rücker, G.; Luckas, K. H. Z. Rechtsmed. 1971, 68, 45–52; (e) Holmstead, R. L.; Casida, J. E. J. Assoc. Off. Anal. Chem. 1974, 57, 1050–1055; (f) Stan, H.-J. Fresenius' Z. Anal. Chem. 1977, 287, 104–111; (g) Stan, H.-J.; Abraham, B.; Jung, J.; Kellert, M.; Steinland, K. Fresenius' Z. Anal. Chem. 1977, 287, 271–285; (h) Busch, K. L.; Bursey, M. M.; Hass, J. R.; Sovocool, G. W. Appl. Spectrosc. 1978, 32, 388–399; (i) Stan, H.-J.; Kellner, G. Biomed. Mass Spectrom. 1982, 9, 483–492; (j) Wilkins, J. P. G. Pestic. Sci. 1990, 29, 163–181.
3. Hummel, S. V.; Yost, R. A. Org. Mass Spectrom. 1986, 21, 785–791.
4. Roach, J. A. G.; Andrzejewski, D. Chem. Anal. (N.Y.) 1987, 91, 187–210.
5. Roach, J. A. G.; Carson, L. J. J. Assoc. Off. Anal. Chem. 1987, 70, 439–442.
6. Zeller, L. C.; Farrell, J. T.; Kenttämaa, H. I.; Kuivalainen, T. J. Am. Soc. Mass Spectrom. 1993, 4, 125–134.
7. Melnikov, N. N.; Mandelbaum, Ya. A.; Lomakina, V. I.; Bakanova, Z. M., Zh. Obshch. Khim. 1956, 26, 2577–2579; Chem. Abstr. 1957, 51, 1825b.
8. Pitt, L. S. U.S. Pat. 4,035,490, 1977; Chem. Abstr. 1977, 87, 97422w.
9. Kornblum, N.; Lurie, A. P. J. Am. Chem. Soc. 1959, 81, 2705–2715.
10. Britton, E. C.; Blair, E. H. U.S. Patent 2,922,811, 1960; Chem. Abstr. 1960, 54, 9848h.
11. Tabor, E. J. U.S. Patent 2,928,864, 1960; Chem. Abstr. 1960, 54,18438f.
12. Kenttämaa, H. I.; Cooks, R. G. J. Am. Chem. Soc. 1985, 107, 1881–1886.
13. Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian 92, Revision C, Gaussian, Inc., Pittsburgh, PA, 1992.
14. Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1, link 607 in Gaussian 92.
15. Harrison, A. G. Chemical Ionization Mass Spectrometry; CRC Press: Boca Raton, FL, 1992.
16. Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. J. Phys. Chem. Ref. Data 1988, 17 (Suppl. 1).
17. Cooks, R. G.; Gerrard, A. F. J. Chem. Soc. B 1968, 1327–1333.
18. Eto, M. Organophosphorus Pesticides: Organic and Biological Chemistry; CRC Press: Cleveland, OH, 1977.