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

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The gas-phase ion chemistry of protonated *O,O*-diethyl *O*-aryl phosphorothionates was studied with tandem mass spectrometric and ab initio theoretical methods. Collision-activated dissociation (CAD) experiments were performed for the $[M + H]^+$ ions on a triple quadrupole mass spectrometer. Various amounts of internal energy were deposited into the ions upon CAD by variation of the collision energy and collision gas pressure. In addition to isobutane, deuterated isobutane C_4D_{10} also was used as reagent gas in chemical ionization. The daughter ions $[M + H - C_2H_4]^+$ and $[M + H - 2C_2H_4]^+$ dominate the CAD spectra. These fragments arise via various pathways, each of which involves γ-proton migration. Formation of the terminal ions $[M + H - 2C_2H_4 - H_2O]^+$, $[M + H - 2C_2H_4 - H_2S]^+$, $[ZPhOH_2]^+$, $[ZPhSH_2]^+$, and $[ZPhS]^+$ [Z = substituent(s) on the benzene ring] suggests that (1) the fragmenting $[M + H]^+$ ions of *O,O*-diethyl *O*-aryl phosphorothionates have protons attached on the oxygen of an ethoxy group and on the oxygen of the phenoxy group; (2) thiono-thiolo rearrangement by aryl migration to sulfur occurs; (3) the fragmenting rearranged $[M + H]^+$ ions have protons attached on the oxygen of an ethoxy group and on the sulfur of the thiophenoxy group. To get additional support for our interpretation of the mass spectrometric results, some characteristics of three protomers of *O,O*-diethyl *O*-phenyl phosphorothionate were investigated by carrying out ab initio molecular orbital calculations at the RHF/3-21G* level of theory. *(J Am Soc Mass Spectrom 1996, 7, 189–197)*

In agriculture, *O,O*-dialkyl *O*-aryl phosphorothionates are widely used as insecticides. They comprise one of the most important classes of organophosphorus pesticides. Generally the alkyl group is methyl or ethyl, whereas there is wide variation in the substituents on the benzene ring.

The *O,O*-dialkyl *O*-aryl phosphorothionates have been studied by mass spectrometry via a variety of ionization techniques [1]. However, only a few publications that deal with the results obtained from collision-activated dissociation tandem mass spectrometry (CAD-MS/MS) experiments have appeared previously [2–6]. The $[M + H]^+$ ions of *O,O*-dimethyl *O*-aryl phosphorothionates were reported to lose neutral methanol, whereas the *O,O*-diethyl *O*-aryl phosphorothionates were reported to lose neutral ethene [2–4]. Ions characteristic to the aryl group in the CAD spectra of the $[M + H]^+$ ions of *O,O*-diethyl *O*-aryl phosphorothionates included $[ZPhSH_2]^+$ and $[ZPhOH_2]^+$ (Z = substituent on the benzene ring) [3]. Multiple stage mass spectrometry (MS^3) has been used to examine the structures of some low mass fragment ions

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commonly produced upon collisional activation of the molecular ions of *O,O*-dialkyl *O*-aryl phosphorothionates [5]. The experiments were carried out on a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. Recently, we published a chemical ionization (CI) CAD-MS/MS study on a series of *O,O*-dimethyl *O*-aryl phosphorothionates [6]. The experiments were carried out with a triple stage quadrupole mass spectrometer. On the basis of the results obtained from the energy- and pressure-resolved CAD experiments, it was concluded that chemical ionization produces a collection of unrearranged and rearranged ions with the extra proton at several ion sites. The CAD spectra exhibited an abundant fragment ion $[M + H - CH_3OH]^+$. The origin of the hydroxy proton in the neutral methanol fragment was in most cases not the reagent gas, isobutane, but surprisingly the phenyl group of phosphorothionates. This was shown by using deuterated isobutane (C_4D_{10}) as reagent gas in chemical ionization.

CI CAD-MS/MS in combination with gas chromatography (GC) offers a fast and selective method for reliable environmental organic analysis. However, the fragmentation reactions of protonated *O,O*-diethyl *O*-aryl phosphorothionates are currently not well established. This article reports a detailed study of the collision-activated dissociation reactions performed on a triple quadrupole mass spectrometer for the $[M + H]^+$ ions of five *O,O*-diethyl *O*-aryl phosphorothionates. Two of the compounds are commercial insecticides (parathion and dichlofenthion); the others have been studied as potential pesticides. The dissociation of the $[M + H]^+$ ions also was studied by energy- and pressure-resolved CAD experiments. Isobutane and deuterated isobutane C_4D_{10} were used as the reagent gases in chemical ionization.

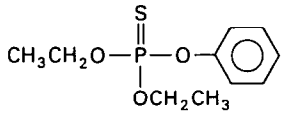
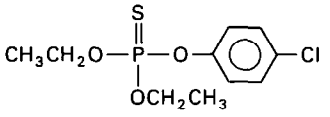
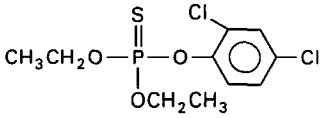
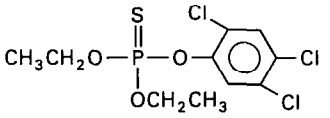
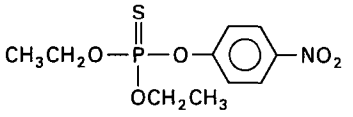
Theoretical ab initio molecular orbital calculations at the RHF/3-21G* level of theory were performed to evaluate the electronic properties and stability order of three protomers of *O,O*-diethyl *O*-phenyl phosphorothionate **1**.

Experimental

Chemicals

The structures of the *O,O*-diethyl *O*-aryl phosphorothionates studied, together with their chemical names, common names, molecular weights, and reference numbers are given in Table 1. The commercial organophosphorus pesticides dichlofenthion and parathion were obtained from the State Institute of Agricultural Chemistry (Finland). *O,O*-Diethyl *O*-phenyl phosphorothionate (**1**), *O,O*-diethyl *O*-4-chlorophenyl phosphorothionate (**2**), and *O,O*-diethyl *O*-(2,4,5-trichlorophenyl) phosphorothionate (**4**) were synthesized by the reaction of *O,O*-diethoxy phosphorochloridothionate and appropriate sodium phenoxide. The methods for synthesis of compounds **1** [7, 8] and **4** [7, 9] were described earlier. Compound **2** was prepared by the method described for **4** [7, 9]. Compounds **1**, **2**, and **4** were purified by vacuum distillation. The purity of all the compounds was confirmed

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

Chemical name; common name	MW	Number of compound	Structure
O,O-diethyl *O*-phenyl phosphorothionate	246	**1**	
O,O-diethyl *O*-4-chlorophenyl phosphorothionate	280	**2**	
O,O-diethyl *O*-(2,4-dichlorophenyl) phosphorothionate; dichlofenthion	314	**3**	
O,O-diethyl *O*-(2,4,5-trichlorophenyl) phosphorothionate	348	**4**	
O,O-diethyl *O*-4-nitrophenyl phosphorothionate; parathion	291	**5**	

by gas chromatography (GC) and nuclear magnetic resonance (NMR) spectroscopy. The proton noise decoupled ^{31}P-{1H} NMR spectra for *O,O*-diethyl *O*-aryl phosphorothionates were recorded at 40 MHz, and showed ^{31}P chemical shifts distributed between 62.00 and 63.14 ppm [relative to the external standard $P(OH)_4^+ClO_4^-$ in D_2O].

Instrumentation

Low energy collision-activated dissociation (CAD) 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. The temperature of the ion source was 120 °C. The electron energy was 150 eV and the emission current was 0.3 mA. Isobutane (Aga Co., Germany; purity 99.95%) 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_4D_{10} (Cambridge Isotope Laboratories, Woburn, MA, 99% deuterium) as reagent gas. Argon (Aga Co., purity 99.998%) was used as the collision gas in the center quadrupole for the CAD experiments. The daughter spectra were recorded by using 20-eV collision energy and 0.8-mtorr pressure. The collision energy was defined by the axial dc offset voltage of Q2 referenced to the ion source. The collision gas pressure was measured by the thermocouple gauge connected into the collision gas inlet. The samples were introduced through a Finnigan MAT 9611 gas chromatograph interfaced by direct coupling to the mass spectrometer. The samples were run in an SE-54 silica capillary column (HNU-Nordion, Finland; 25 m, 0.32 mm, 0.25 μm) with an injector temperature of 220 °C and helium carrier gas at a flow rate of about 1.5 mL min^{-1}. The temperature program started at 60 °C (1 min) and had a final temperature of 250 °C (15 °C min^{-1}). The interface temperature was 260 °C. The energy-resolved experiments were performed on the protonated compounds **1–5** by recording successive daughter spectra as the collision energy was increased in ~ 5-eV intervals from 5 up to 30 eV (E_{lab}), at the collision gas pressure of 0.8 mtorr. In the energy-resolved experiments the samples were introduced by direct inlet [direct exposure probe (DEP), Finnigan MAT] by heating the filament with electric current. The heating rate was 2×10^{-3} A s^{-1}. The pressure-resolved experiments were performed on the $[M + H]^+$ ions of compounds **1** and **2** at collision gas pressure of 0.1, 0.4, 0.6, and 0.8 mtorr, at a collision energy of 20 eV. In the pressure-resolved experiments, the samples were introduced through the gas chromatograph. 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 molecular orbital calculations were carried out by the Gaussian 92 program [10] 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. Natural bond orbital (NBO) analyses were performed for each species to evaluate the electronic properties [11].

Results and Discussion

The ions $[M + H]^+$ were produced with isobutane CI, the plasma of which contains tert-butyl cation $[t\text{-}C_4H_9]^+$ (97% relative abundance) and isopropyl cation $[C_3H_7]^+$ (3%). The proton affinity (PA) of isobutene (the conjugate base of the Brönsted acid $[t\text{-}C_4H_9]^+$) is 819.6 kJ mol^{-1} and the PA of propene (the conjugate base of the Brönsted acid $[C_3H_7]^+$) is 751.0 kJ mol^{-1} [12]. Under isobutane CI conditions, the phosphorothionates studied form intense $[M + H]^+$ ions with little fragmentation. Also the deuterated isobutane C_4D_{10} CI spectra were recorded for compounds **1** and **2**. Comparison of the intensity ratios of the isotopic patterns of the $[M + H]^+$ and $[M + D]^+$ ions in the C_4H_{10} and C_4D_{10} CI spectra, respectively, showed that no proton–deuteron exchange occurs upon CI when C_4D_{10} is used as reagent gas. To get more detailed information about the fragmentation pathways, the CAD spectra also were recorded for compounds **1–5** by using deuterated isobutane C_4D_{10} as reagent gas in chemical ionization.

The initial protonation produces $[M + H]^+$ ions with an excess of 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 neutral species of the reagent plasma, the $[M + H]^+$* ions may undergo collisional stabilization that produces a collection of $[M + H]^+$ ions [12], where the proton may be attached on different basic molecular sites. The protomer composition is not necessarily governed by thermodynamic control. The protomer composition may be dominated by competing rates of formation of the possible protomers, and the thermodynamically favored site of protonation may differ from the kinetically favored site [12]. 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 affinity of triethylphosphorothionate $(CH_3CH_2O)_3PS$ is approximately 920 kJ mol^{-1}. The value is estimated by using the proton affinities of $(CH_3O)_3PO$ (887.0 kJ mol^{-1}), $(CH_3O)_3PS$ (897.5 kJ mol^{-1}), and $(CH_3CH_2O)_3PO$ (≈ 910 kJ mol^{-1}) [13]. The proton affinities of benzene, chlorobenzene, and nitrobenzene are 758.6, 760.2, and 809.2 kJ mol^{-1}, respectively [13]. Accordingly, the thermodynamically favored protonation site of *O,O*-diethyl *O*-phenyl, *O,O*-diethyl *O*-chlorophenyl, and *O,O*-diethyl *O*-nitrophenyl phosphorothionates is the

phosphorothionate moiety when isobutane is used as reagent gas in CI.

Ab Initio Calculations

Ab initio theoretical calculations with the 3-21G* basis set were performed to investigate the structures and the electronic properties of three protomers of compound **1** (**a**, **b**, **c**) at the RHF level of theory. The protomer **a** has a proton on the sulfur, the protomer **b** has a proton on the oxygen of an ethoxy group, and the protomer **c** has a proton on the oxygen of the phenoxy group. The optimized geometries for protomers **a**, **b**, and **c** are shown in Figure 1. The RHF/3-21G* vibrational frequencies were computed for each optimized species to characterize them as true minima. No imaginary frequencies were found. Thus each structure represents a true energy minimum. Figure 2 summarizes the calculated bond lengths (angstroms) and ab initio energies *E*(RHF). According to present calculations, for protonated **1** the lowest energy protomer is **a**. Protomer **a** is 76.3 kJ mol^{-1} and protomer **b** is 6.4 kJ mol^{-1} more stable than protomer **c**. Consequently, the thermodynamically preferred protonation site is the sulfur. To get additional support from the theoretical point of view for our interpretation of the experimental mass spectrometric results, we extended these calculations to determine the bond orders, bond strengths, and natural charges of protonated **1**. Natural bond orbital analyses (NBO) were performed to protomers **a**, **b**, and **c**. The occupancies obtained for the bonding orbitals in phoshorus–sulfur bonds are 1.991 electrons (**a**), 1.995 electrons (**b**), and 1.866 electrons (**c**). The extent of the $p\pi$-$d\pi$ interaction that contributes to the phosphorus–sulfur bonding was found to be negligible for all protomers. These results suggest that the phosphorus–sulfur bond can be viewed as a dipolar single σ-bond $P^+—S^-$ rather than as P=S with $p\pi$-$d\pi$ character. The usual practice to describe bonding between phosphorus and oxygen and sulfur as $R_3P = X$ has been criticized in many publications [14]. Our natural population analysis gave results that are very similar to those obtained for *O,O*-dimethyl *O*-phenyl phosphorothionates in our previous study [6]. For protomers **a**, **b**, and **c**, there are remarkable excesses of electrons in the ethoxy oxygens (natural charge −0.830 to −0.925), in the phenoxy oxygens (natural charge −0.789 to −0.886), and in the sulfur (natural charge −0.239 to −0.573), whereas the phosphorus bears high positive charge (natural charge +2.185 to +2.421). 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 coordinated to the $P^+—S^-$ group. The ab initio calculated donor–acceptor interaction energies [E(2) in NBO notation] between oxygen lone pairs (lp) and lp*-orbitals of phosphorus are presented in Table 2.

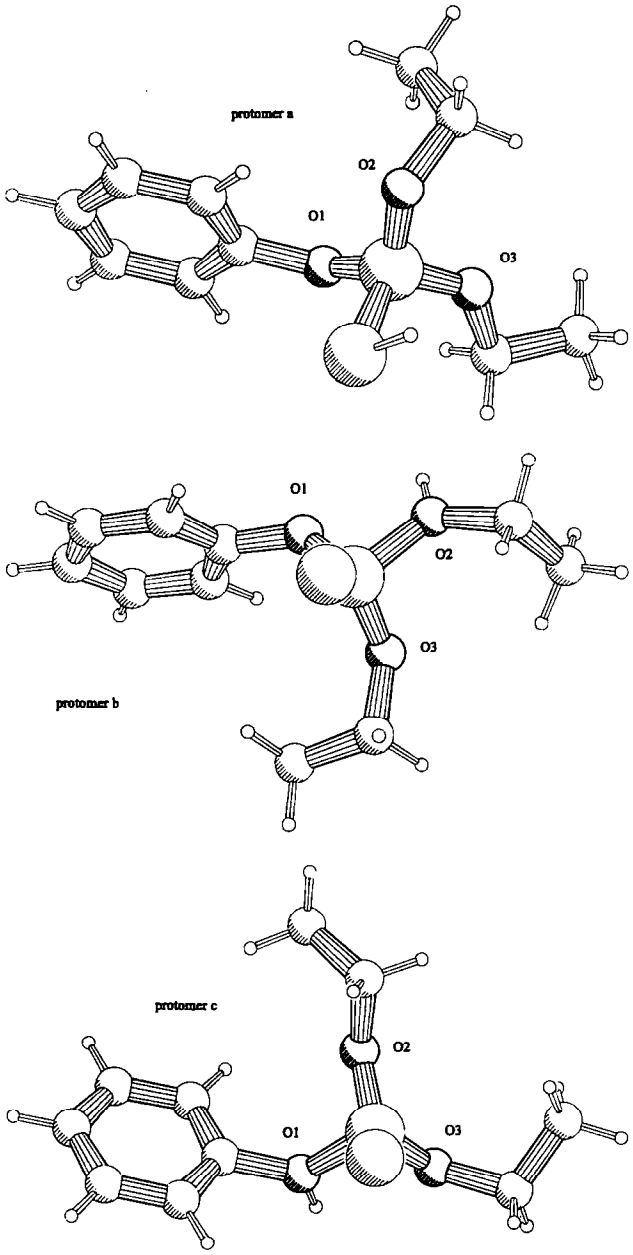


Figure 1. 3-21G*-optimized geometries for protomers **a**, **b**, and **c** of *O,O*-diethyl *O*-phenyl phosphorothionate (**1**).

Table 2. The sums for the electron donor–acceptor interaction energies[a] (kilojoules per mole) 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	2537.2	2744.9	2755.2
b	2659.5	1354.3	2701.0
c	866.6	1641.3	2377.5

[a] E(2) in NBO notation.

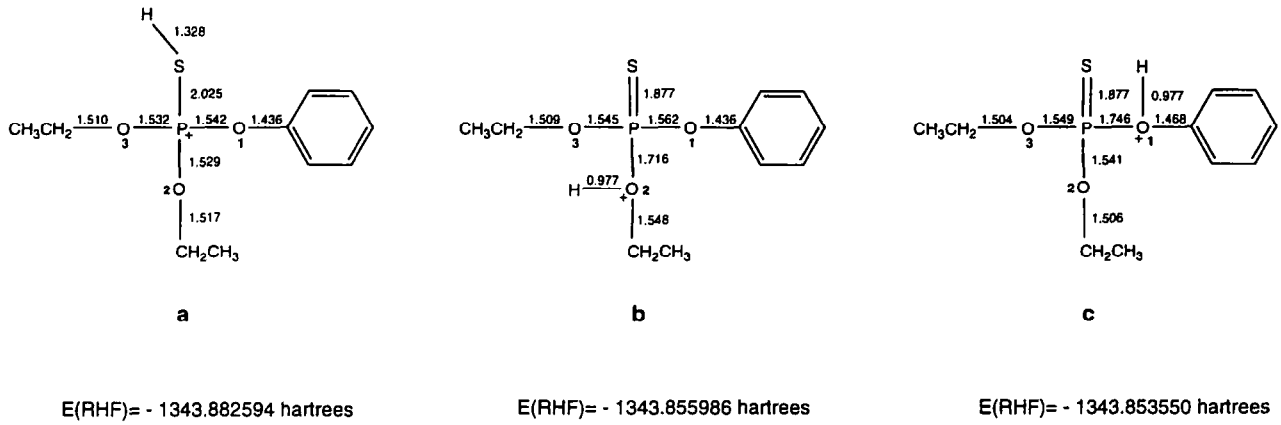


Figure 2. Computed bond lengths (angstroms) and *E*(RHF) energies (hartrees) for protomers **a**, **b**, and **c** of compound **1**.

Fragmentation of the [M + H]⁺ Ions

The 20-eV CAD-MS/MS daughter ion spectra of the ions $[M + H]^+$ of the phosphorothionates **1–5** are presented in Table 3. Because the low energy CAD is particularly sensitive to collision energy and collision gas pressure, these parameters were changed to change the energy deposited in the ion $[M + H]^+$. Figure 3 shows the energy-resolved curves for compounds **1**, **2**, and **5**. Figure 4 shows the pressure-resolved curves for **1** and **2**. An interesting observation is that the substituents have no significant effect on the relative abundance percent (RA %) of the fragment ions: the profiles of the energy-resolved and also the pressure-resolved curves are quite similar. This implies that the reaction centers are remote from the benzene ring.

Unlike the protonated *O,O*-dimethyl *O*-aryl phosphorothionates, the protonated *O,O*-diethyl *O*-aryl phosphorothionates do not fragment upon CAD by loss of a neutral alcohol, phenol, or thiophenol (the dissociation product from the thiono-thiolo rearranged precursor ion) [6]. Instead, the protonated *O,O*-diethyl *O*-aryl phosphorothionates dissociate to produce the ions $[M + H - C_2H_4]^+$ and $[M + H - 2C_2H_4]^+$ as main daughter ions. The loss of ethene molecules is common for all phosphorus ester ions that contain ethyl groups. For example, triethyl phosphate fragments upon electron impact via the loss of ethene molecules [15]. Protonated triethyl phosphate formed by atmospheric pressure ionization dissociates upon CAD by the loss of ethene molecules [16]. The energy-resolved curves (Figure 3) show that at 5-eV collision energy the RA% of the $[M + H - 2C_2H_4]^+$ ions is somewhat lower than that of the $[M + H - C_2H_4]^+$ ions, whereas at the region 10–30 eV the RA% of the $[M + H - 2C_2H_4]^+$ ions increases strongly at the expense of the RA% of the $[M + H - C_2H_4]^+$ ions. The same behavior also was observed for these two ions in the pressure-resolved curves (Figure 4). On the basis of these results it can be concluded that the elimination of the ethene molecules is a very favorable reaction.

At higher collision energies, the CAD spectra exhibit minor fragment ions $[M + H - 2C_2H_4 - H_2S]^+$ and $[ZPhOH_2]^+$ (Z = substituent(s) on the benzene ring). This suggests that the fragmenting $[M + H]^+$ ions carry the extra proton on the oxygen of an ethoxy group (Scheme I) and on the oxygen of the phenoxy group (Scheme II). The loss of the first C_2H_4 molecule is proposed to proceed by a rearrangement reaction where a proton from the γ-position transfers to the basic thiophosphoryl sulfur (Schemes I and II) through the sterically favorable six-membered cyclic transition

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

	Ion *m/z* (relative abundance)[a]								
Compound	$[M+H]^+$	$[M+H-2C_2H_4]^+$	$[M+H-C_2H_4]^+$	$[M+H-2C_2H_4-H_2O]^+$	$[ZPhOH_2]^+$	$[ZPhSH_2]^+$	$[M+H-2C_2H_4-H_2S]^+$	$[ZPhS]^+$	Other Ions
1	247(24)	191(100)	219(16)	173(16)	95(7)	111(6)	157(1)	109(3)	—
2	281(19)	225(100)	253(16)	207(8)	129(5)	145(6)	191(1)	143(3)	97(2)
3	315(20)	259(100)	287(17)	241(5)	163(3)	179(5)	225(3)	—	97(4), 223(1)
4	349(19)	293(100)	321(18)	275(4)	197(5)	213(6)	259(3)	—	97(6)
5	292(15)	236(100)	264(12)	218(3)	140(4)	156(4)	—	—	94(1), 97(2), 109(1), 110(1), 125(1), 190(3)

[a] Only relative abundances ≥ 1% are reported.

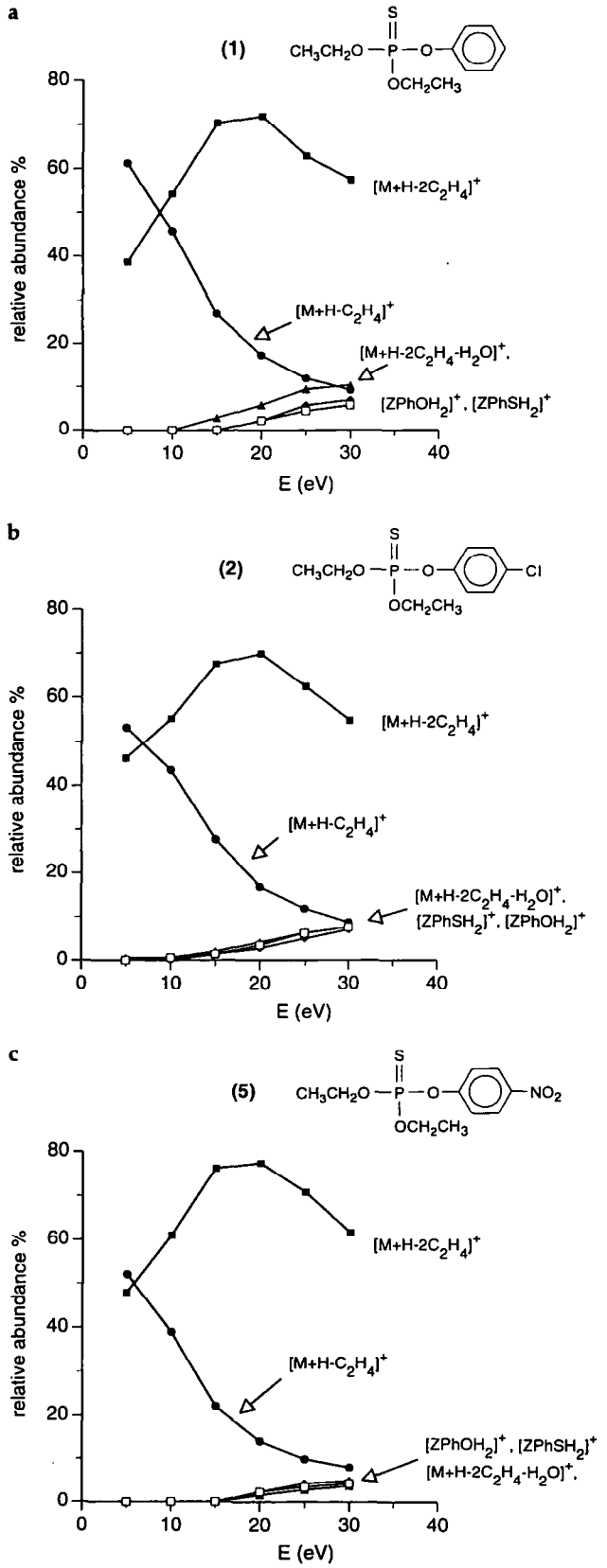


Figure 3. Energy-resolved curves of the $[M + H]^+$ ions of *O,O*-diethyl *O*-aryl phosphorothionates: (a) **1**; (b) **2**; (c) **5**. The total ion current was calculated by excluding the parent ion.

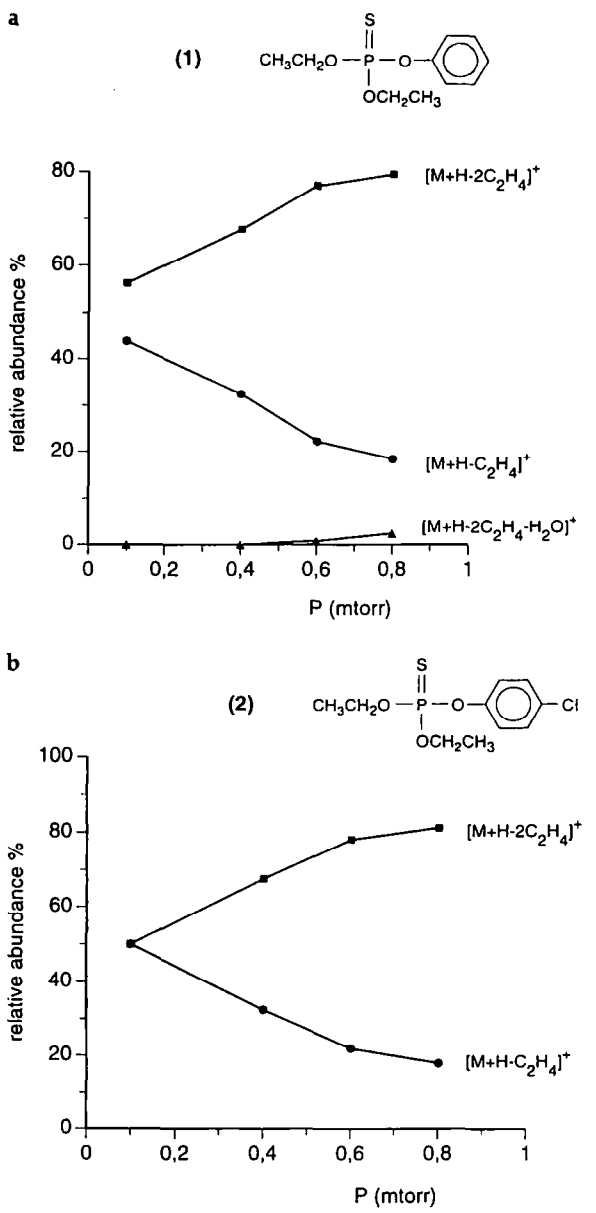
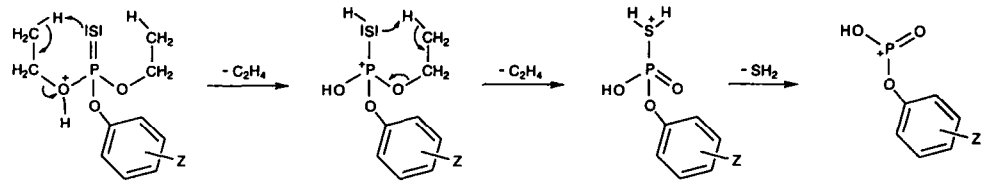


Figure 4. Pressure-resolved curves of the $[M + H]^+$ ions of *O,O*-diethyl *O*-aryl phosphorothionates: (a) **1**; (b) **2**. The total ion current was calculated by excluding the parent ion.

state followed by the thermodynamically favored elimination of a neutral ethene molecule. The results obtained from the ab initio calculations support the presented fragmentation pathways: the sulfur has a remarkable excess of electrons that results in a great tendency to accept γ-protons. The pathway presented in Schemes I and II is a McLafferty-like rearrangement where a γ-proton transfers onto the formally unsaturated group. Elimination of the second C_2H_4 is proposed to occur also via the cyclic transition state. A lone electron pair of the sulfur of the $[M + H - C_2H_4]^+$ ion accepts the γ-proton, which results in

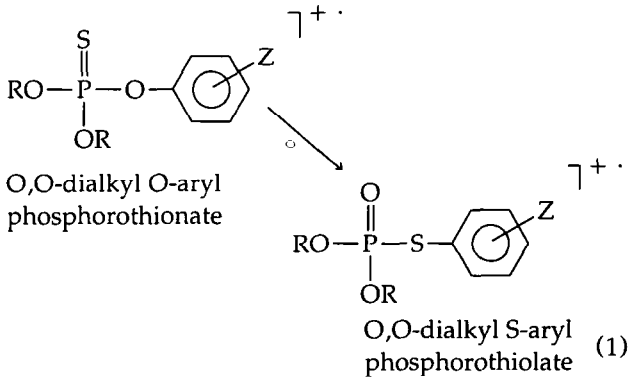


b

Scheme I

formation of the ion $[M + H - 2C_2H_4]^+$ that can lose SH_2 as shown in Scheme I. The protonated phenol ion is assumed to arise from the $[M + H - C_2H_4]^+$ ion by a rearrangement reaction where the γ-proton migrates to the phenoxy oxygen (Scheme II). With C_4D_{10} as reagent gas in chemical ionization, the *O*-protonated phenol ions had one mass unit higher mass value in their respective CAD spectra. This observation excludes the following conceivable fragmentation pathway: the loss of the first C_2H_4 could occur from protomer **b** by transfer of a γ-proton to the oxygen of the phenoxy group followed by the loss of the second C_2H_4 as presented in Scheme II.

In the liquid phase, neutral *O,O*-dialkyl *O*-aryl phosphorothionates isomerize at high temperatures to some extent (dependent on the heating temperature and time) into *S*-alkyl phosphorothiolates. Aryl groups do not transfer at all [17]. Upon electron impact, phosphorothionate esters also have been reported to undergo a thiono-thiolo rearrangement reaction. In addition to the alkyl group, the aryl group also migrates to sulfur (see reaction 1) [18]:

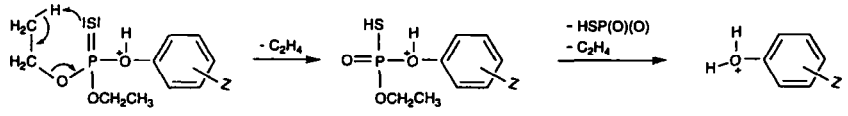


O,O-dialkyl O-aryl phosphorothionate

O,O-dialkyl S-aryl phosphorothiolate (1)

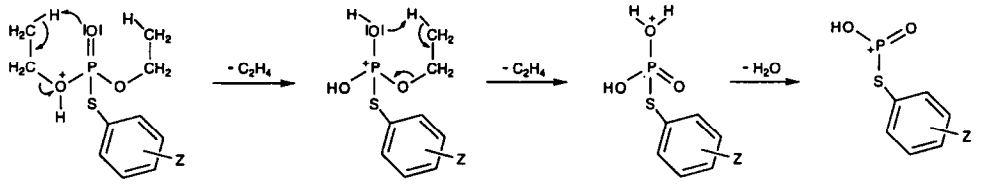
In the CI CAD-MS/MS experiment, the CAD spectrum of the $[M + H]^+$ ions of *O,O*-diethyl *O*-4-nitrophenyl phosphorothionate **5** (parathion) has been reported to exhibit the ion $[ZPhSH_2]^+$, which is an indication of the thiono-thiolo rearrangement reaction [3]. In our experiments, the CAD spectra of the protonated *O,O*-diethyl *O*-aryl phosphorothionates (Table 3) exhibited the fragment ions $[M + H - 2C_2H_4 - H_2O]^+$, $[ZPhSH_2]^+$, and $[ZPhS]^+$, which suggests that the thiono-thiolo rearrangement by aryl migration to sulfur occurs also under the present conditions. However, these fragmentation products are formed only at higher collision energies (Figure 3). This could imply that the isomerization occurs for the protonated $[M + H]^+$ ions as a result of the increase in the internal energy deposited into the ions upon collisional activation. Alternatively, the internal energy obtained upon isobutane CI may be high enough to allow unimolecular isomerization that results in a collection of rearranged and unrearranged $[M + H]^+$ ions. This was concluded by us to occur for the *O,O*-dimethyl *O*-aryl phosphorothionates in our earlier study [6]. Unfortunately, on the basis of the present results it is not possible to conclude where the thiono-thiolo rearrangement reaction occurs for the protonated ethyl compounds studied.

The fragmentation proposed for the rearranged $[M + H]^+$ ions—the protonated *O,O*-diethyl *S*-aryl phosphorothiolates—are presented in Schemes III and IV. The loss of ethene proceeds by a rearrangement reaction where a proton from the γ-position transfers to the oxygen as shown in Schemes III and IV. The most plausible explanation for the formation of the ion $[M + H - 74]^+$ is the elimination of two ethene molecules and one water molecule from the $[M + H]^+$ ion with the proton on the oxygen of an ethoxy group as shown in Scheme III. Another conceivable mechanism for the production of the ion $[M + H - 74]^+$ is a loss of CH_3CH_2OH and ethene molecules from the ion $[M + H]^+$. However, the former proposition gains support from a finding that, with C_4D_{10} as the reagent gas, the $[M + H - 74]^+$ ions had one mass unit higher mass value in their respective CAD spectra, whereas according to the latter proposition the deuteron would

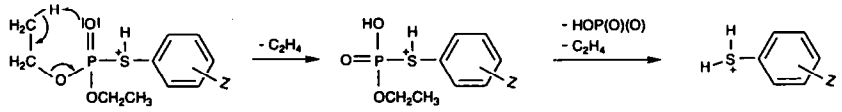


c

Scheme II



Scheme III



Scheme IV

be expected to reside on the ethanol-leaving group. Further evidence for the former proposition comes from the energy-resolved curves (Figure 3): at higher collision energies the RA% of the ions $[M + H - C_2H_4]^+$ and $[M + H - 2C_2H_4]^+$ decreases and the RA% of the ion $[M + H - 2C_2H_4 - H_2O]^+$ increases. The 20-eV CAD spectra of all the compounds studied exhibited the ion $[ZPhSH_2]^+$. With C_4D_{10} as reagent gas, the deuteron resides on the ion $[ZPhSHD]^+$. The mechanism proposed for the formation of this ion (Scheme IV) is analogous to that presented for the formation of ion $[ZPhOH_2]^+$ (Scheme II).

In the case of compound **1**, the structure of the ion of m/z 109 could be $[PhS]^+$ or $(CH_3CH_2O)(HO)PO^+$. Isotope data were used to resolve which of the ions is in question. The 20-eV CAD spectrum was measured for the ion $[M + H + 2]^+$ that contains the isotopic sulfur atom ^{34}S. Comparison of this spectrum with the spectrum obtained for the $[M + H]^+$ ion revealed that the m/z 109 ion contains sulfur: instead of the m/z 109 ion, the spectrum of the $[M + H + 2]^+$ ion exhibited an ion at m/z 111. On the basis of this result, the structure of the m/z 109 ion is most propably $[PhS]^+$.

Conclusions

The loss of ethene molecules common for all phosphorus ester ions that contain ethyl groups also was observed for the protonated *O,O*-diethyl *O*-aryl phosphorothionates upon CAD. The proposed precursor ions for the fragment ion $[M + H - C_2H_4]^+$ are (1) *O,O*-diethyl *O*-aryl phosphorothionate with the proton on the oxygen of an ethoxy group and on the oxygen of the phenoxy group and (2) rearranged *O,O*-diethyl *O*-aryl phosphorothionate (*O,O*-diethyl *S*-aryl phosphorothiolate) with the proton on the oxygen of an ethoxy group and on the sulfur of the thiophenoxy group. The losses of the C_2H_4 molecules are suggested to proceed by rearrangement reactions where a proton from the γ-position transfers to the sulfur and to the oxygen via the six-membered cyclic transition state followed by α,β-bond cleavage. According to the results obtained from the ab initio calculations performed for the three protomers of compound **1**, sulfur has a remarkable excess of electrons. This explains the great tendency of this atom to accept γ-protons, which results in the favorable loss of C_2H_4. The CAD spectra of the studied compounds exhibited the ion $[ZPhOH_2]^+$. With C_4D_{10} as reagent gas in CI, the fragment ions $[ZPhOH_2]^+$ had one mass unit higher mass value in their respective CAD spectra. This suggests that the precursor ion for $[ZPhOH_2]^+$ has the proton on the oxygen of the phenoxy group. The formation of the terminal ions $[M + H - 2C_2H_4 - H_2O]^+$, $[ZPhSH_2]^+$, and $[ZPhS]^+$ suggests that the thiono-thiolo rearrangement by aryl migration to sulfur occurs under the present conditions. This rearrangement could occur upon protonation in the ion source or upon collision with the target gas in Q2. However, the results obtained in this study cannot distinguish among these possibilities. The fragmentation behavior is not significantly influenced by the chloro and nitro substituents at the benzene ring as can be seen from the profiles of the energy- and pressure-resolved curves. This implies that the reaction centers in collision-activated dissociation are remote from the benzene ring.

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