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Long-Lived Radical Cations of Simple Organophosphates Isomerize Spontaneously to Distonic Structures in the Gas Phase

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Abstract: The structures and relative stabilities of the long-lived radical cations formed upon removal of an electron from simple organophosphorus esters have been examined in the gas phase. Different mass spectrometric methods were used to investigate the relative heights of the energy barriers for fragmentation and isomerization. Reference ions were generated by dissociative ionization of suitable precursor ions. Thermoneutral hydrogen/deuterium exchange reactions with deuterated ammonia proved to be a useful tool in the identification of distonic radical cations characterized by separate radical and charge sites: distonic ions readily exchange one hydrogen atom with deuterium, while ions with the conventional structure are unreactive toward deuterated ammonia. The results obtained explicitly demonstrate that the long-lived radical cations of organophosphates spontaneously isomerize to more stable distonic structures in the gas phase. In sharp contrast to ionized organophosphates, the long-lived radical cation of trimethyl phosphorothionate is stable in the gas phase. On the basis of a revised ionization energy of 8.5–8.7 eV for trimethyl phosphorothionate, the isomerization to a distonic form is estimated to be endothermic for this radical cation.

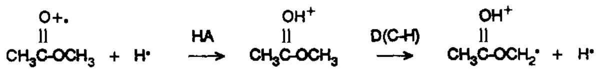
Introduction

Ions with formally separate radical and charge sites (*distonic ions*[1]) have been the focus of numerous recent research projects. The interest in these ions arises, in part, from the discovery in 1982 that some simple distonic ions (e.g., $^{\bullet}CH_2OH_2^+$) are more stable than their conventional isomers, the radical cations generated by removal of an electron from a stable neutral molecule (e.g., $CH_3OH^{\bullet+}$).[2] Distonic ions are now known to be common as intermediates and products in unimolecular reactions of isolated organic radical cations in the gas phase as well as in low-temperature halocarbon matrices.[1-4] For example, the radical cation of methyl acetate has been proposed to isomerize to its distonic form prior to dissociation in the gas phase.[3-6]

Phosphorus-containing distonic ions have received relatively little attention thus far.[1,7] However, rearrangement of the conventional radical cations of organophosphorus esters to distonic structures should be significantly more exothermic than for the analogous carbon esters since the hydrogen atom affinities of the former are higher (see Scheme I; the hydrogen atom affinities (HA) for ionized methyl acetate and ethyl acetate are 121 and 118 kcal/mol, respectively, and for ionized trimethyl phosphate and triethyl phosphate 129 kcal/mol;[8] values for other organophosphorus radical cations are listed in Table I). In support of these considerations, recent results obtained using electron spin resonance spectroscopy[7c,d] suggest that the radical cation of trimethyl phosphate irreversibly rearranges through a hydrogen atom transfer in $CFCl_3$ at 77 K. Moreover, the internally excited radical cation of dimethyl methylphosphonate has been demonstrated[7b,e] to rearrange to its distonic and enol isomers in the gas phase (Scheme II). These rearrangement reactions were proposed[7e] to be significantly more exothermic ($\Delta H_{rxn} = -43$ kcal/mol) than the related reactions for methyl acetate ($\Delta H_{rxn} = -8$ kcal/mol[5,6]), and the barriers for isomerization were estimated to be smaller for the phosphorus compound (less than 16 kcal/mol for the phosphorus ester, ≤23 kcal/mol for ionized methyl acetate[4]).

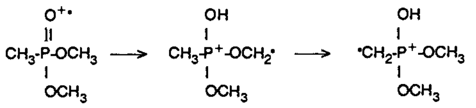
We report here the first investigation on the structures of the *long-lived, low-energy* radical cations of organophosphorus esters in the gas phase. The results obtained explicitly demonstrate that *the radical cations of simple organophosphates do not exist as conventional structures* but that they spontaneously isomerize to more stable distonic forms. This, however, does not apply to ionized thioesters which are stable in the gas phase.

Scheme I



$$\mathrm{CH_3\overset{O+\cdot}{\overset{\|}{C}}\text{-}OCH_3 + H^{\cdot} \xrightarrow{HA} CH_3\overset{OH^+}{\overset{\|}{C}}\text{-}OCH_3 \xrightarrow{D(C\text{-}H)} CH_3\overset{OH^+}{\overset{\|}{C}}\text{-}OCH_2^{\cdot} + H^{\cdot}}$$

Scheme II



$$\mathrm{CH_3\text{-}\underset{\underset{OCH_3}{|}}{\overset{\overset{O^{+\cdot}}{\|}}{P}}\text{-}OCH_3 \longrightarrow CH_3\text{-}\underset{\underset{OCH_3}{|}}{\overset{\overset{OH}{|}}{P^+}}\text{-}OCH_2^{\cdot} \longrightarrow {}^{\cdot}CH_2\text{-}\underset{\underset{OCH_3}{|}}{\overset{\overset{OH}{|}}{P^+}}\text{-}OCH_3}$$

Table I. Thermochemical Values Used in This Work

compound	IE,[a] eV	PA,[a] kcal/mol	HA,[b] kcal/mol
$(CH_3O)_3PO$	9.99	212.0	129
$(C_2H_5O)_3PO$	~9.8	~217	129
$(CH_3O)_3PS$	8.5–8.7[c]	214.5	97–102
$(CH_3O)_3P$	~8.5	220.6	103
$(C_2H_5O)_3P$	~8.4	226[d]	105
$(i\text{-}C_3H_7O)_3P$	~8.3[e]	228[d]	107
$(CH_3)_3P$	8.06	227.1	99
$(C_2H_5)_3P$	8.15	231.7	106
$(CH_3)_3PO$	~9.5	217.1	123
$(CH_3O)_2P(O)CH_3$	10.48[e]		
NH_3	10.16	204	125

[a] Ionization energies (IE) and proton affinities are from ref 8 unless otherwise specified. [b] Hydrogen atom affinities (HA) were calculated using the following equation: HA = PA + IE (kcal/mol) − $IE(H^{\bullet})$; $IE(H^{\bullet})$ = 313.58 kcal/mol.[8] [c] Result obtained in this work. [d] Estimated using a correlation between the proton affinity and ionization energy for trivalent phosphorus esters: PA = 0.853(459 − IE) (see ref 9); all quantities expressed in kcal/mol. [e] Reference 10.

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Table II. Dissociation Products Obtained for Some of the Organophosphorus Ions Studied

Compound Ion	Method[a]	m/z (%)[b]
Trimethyl phosphate		
$M^{+\cdot}$ (m/z 140)	EIMS, ICR	
	20 eV	140(5), 111(2), 110(100), 109(10), 95(12), 93(<5), 80(27), 79(15), 47(4)
	CAD, near single collision conditions, ICR, CE with $CS_2^{+\cdot}$	
	10 eV	110(100), 95(<5), 80(18), 79(14)
	25 eV	110(100), 95(7), 80(33), 79(39)
	CAD, multiple collision conditions, ICR, CE with $CS_2^{+\cdot}$	
	10 eV	110(100), 80(31), 79(29)
	25 eV	110(100), 95(12), 80(73), 79(98), 47(9)
	CAD, EB instrument, 70 eV EI	
	3 keV	111(3), 110(100), 109(5), 95(13), 80(5), 79(11), 65(9)
m/z 110	CAD, near single collision conditions, ICR, 20 eV EI	
	10 eV	95(11), 80(100), 79(70)
	25 eV	95(32), 80(96), 79(100), 65(6), 47(12)
	CAD, multiple collision conditions, QQQ, 70 eV EI	
	20 eV	95(14), 80(12), 79(100), 65(9), 47(36)
	CAD, EB instrument, 70 eV EI	
	3 keV	95(70), 80(60), 79(100), 65(<5), 47(10)
MH^+ (m/z 141)	multiple collision conditions,[c] ICR	
	25 eV	109(100), 79(<5)
Dimethyl n-propyl phosphate		
$M^{+\cdot}$ (m/z 168)	EIMS, EB	
	18 eV	153(5), 140(<5), 139(6), 127(100), 109(13)
	70 eV	153(5), 140(<5), 139(9), 127(100), 110(5), 109(54), 80(<5), 79(7), 96(7), 95(8), 47(<5)
m/z 140	CAD, multiple collision conditions, ICR, 15 eV EI	
	20 eV	110(100), 95(12), 80(83), 79(75)
m/z 139	CAD, EB, 70 eV EI	
	3 keV	110(20), 109(100), 95(5), 80(<5), 79(9), 47(<5)
Triethyl phosphate		
$M^{+\cdot}$ (m/z 182)	EIMS, ICR	
	15 eV	182(3), 155(100), 139(6), 138(8), 127(56), 125(7), 111(6), 109(5), 99(39), 83(5), 82(8), 81(8)
	CAD, near single collision conditions, ICR, 15 eV EI	
	25 eV	155(100), 138(15), 127(83), 99(72), 83(15), 82(18)
	50 eV	155(83), 138(13), 127(76), 125(17), 111(21), 99(100), 83(30), 82(43), 81(22), 65(17)
	CAD, near single collision conditions, ICR, CE with $CS_2^{+\cdot}$	
	25 eV	155(100), 138(<5), 127(51), 111(5), 99(66), 83(5), 82(5)
	CAD, multiple collision conditions, ICR, 15 eV EI	
	25 eV	155(25), 127(31), 111(<5), 99(100), 83(10), 82(7), 81(<5)
	50 eV	155(8), 127(8), 99(100), 83(25), 82(19), 81(56), 65(25)
Diethyl methoxyethyl phosphate		
$M^{+\cdot}$ (m/z 212)	EI, ICR	
	18 eV	182(11), 155(100), 139(13), 127(64), 113(19), 109(6), 99(60), 82(9), 81(19), 73(5), 59(6), 58(73), 47(9), 45(41), 43(9), 31(6), 29(7)
m/z 182	CAD, near single collision conditions, ICR, 18 eV EI	
	20 eV	155(100), 138(15), 127(50), 99(50), 83(20), 82(25)
	50 eV	155(100), 138(20), 127(83), 125(10), 111(20), 99(95), 83(35), 82(60), 65(15)
	CAD, multiple collision conditions, ICR, 15 eV EI	
	25 eV	155(65), 127(41), 99(100), 83(9), 82(7), 81(6), 47(9)
	50 eV	155(17), 127(10), 99(100), 83(16), 82(11), 81(13), 65(6)
	CAD, EB instrument, 70 eV EI	
	3 keV	155(100), 138(11), 127(20), 126(6), 125(11), 99(21), 83(<5), 82(8), 81(5)
Trimethyl phosphorothionate		
$M^{+\cdot}$ (m/z 156)	EIMS, ICR	
	15 eV	156(100), 126(60), 125(4), 93(95), 79(<5), 63(7), 47(<5)
	CAD, multiple collision conditions, ICR, 75 eV EI	
	50 eV	126(16), 125(13), 109(11), 93(100), 63(20), 47(<5)
	75 eV	126(10), 125(16), 109(13), 93(100), 63(20), 47(6)
MH^+ (m/z 157)	CAD, near single collision conditions, ICR	
	50 eV	156(9), 125(100), 94(6), 93(7), 79(13), 47(20)
	75 eV	156(9), 125(100), 93(10), 79(18), 47(26)
m/z 126	CAD, multiple collision conditions, ICR, 70 eV EI	
	25 eV	93(100), 63(34)
Trimethyl phosphite		
$M^{+\cdot}$ (m/z 124)	EIMS, ICR	
	20 eV	124(53), 109(60), 94(32), 93(100), 79(20), 63(22)
	CAD, near single collision conditions, ICR, CE with CS_2	
	25 eV	109(55), 94(40), 93(100), 79(15), 63(20), 47(6)
	50 eV	109(70), 95(10), 94(30), 93(100), 79(20), 63(40), 47(20)
MH^+ (m/z 125)	CAD, near single collision conditions, ICR	
	25 eV	109(10), 93(100), 79(35), 83(15), 47(69)
	50 eV	93(80), 79(50), 83(20), 47(100)
Triethyl phosphite		
$M^{+\cdot}$ (m/z 168)	EI, ICR	
	50 eV	167(10), 166(42), 139(83), 122(27), 121(54), 111(95), 110(9), 109(15), 94(8), 93(50), 91(28), 83(77), 82(87), 81(41), 65(100), 47(20), 45(18)
	CAD, near single collision conditions, ICR, CE with $CS_2^{+\cdot}$	
	25 eV	139(100), 122(46), 111(60), 94(36), 83(80), 82(30), 66(33), 65(41)
	50 eV	139(72), 111(46), 94(33), 83(99), 82(38), 81(27), 66(35), 65(100)

[a] For CAD, the laboratory ion kinetic energy is given; for EI, the electron energy is given. See the Experimental Section for a detailed description of single, near single, and multiple collision conditions in different instruments. [b] Ions with less than 5% relative abundance are not reported unless they are discussed in the paper. [c] 5×10^{-7} Torr of argon, reaction time 100 ms.

Experimental Section

Collision-activated dissociation (CAD) data (Table II) were obtained on several different mass spectrometers. The radical cations were generated by electron ionization (EI) (the results were found to be independent of the electron energy within the range 12–70 eV) or by charge exchange (CE) using $CS_2^{\cdot+}$ reagent ions (recombination energy[8] 10.07 eV). Protonated molecules were generated by self-chemical ionization wherein fragment ions obtained by electron ionization induced dissociation of the sample are used to protonate the neutral sample molecules. All the chemicals were used as received from manufacturers without further purification. Their identity and purity was checked mass spectrometrically. The compounds not available commercially (diethyl pentyl phosphate, diethyl methoxyethyl phosphate, dimethyl propyl phosphate) were synthesized using common laboratory procedures.

High-energy collision-activated dissociation was carried out using two different sector instruments. The ion kinetic energy (collision energy) in the instrument of the MIKES type[11] (BE configuration) was 7 keV. Air was used as the collision target at a nominal pressure of 3×10^{-5} Torr (15–35% main beam attenuation), as measured with an ionization gauge

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Table III. Reaction Rates and Product Distributions Obtained for Ion–Molecule Reactions of Phosphorus Cations

reaction	ionic products (m/z)	branching ratio,[a] %	k^b	$k_{\mathrm{ADO}}{}^c$
$\{(CH_3O)_3PO\}^{\bullet+}$ + $(CH_3O_3)P$	$(CH_3O)_3PH^+$ (125) $(CH_3O)_2P^+$ (93)	90 10	11	15
$(CH_3O)_3POH^+$ + $(CH_3O)_3P$	$(CH_3O)_3PH^+$ (125) $(CH_3O)_2P^+$ (93)	85 15	9.5	15
$\{(C_2H_5O)_3PO\}^{\bullet+}$ + $(CH_3O)_3P$	$(CH_3O)_3PH^+$ (125)	100	13	14
$(C_2H_5O)_3POH^+$ + $(CH_3O)_3P$	$(CH_3O)_3PH^+$ (125)	100	12	14
$(CH_3O)_3PS^{\bullet+}$ + $(CH_3O)_3P$	$(CH_3O)_3P^{\bullet+}$ (124) $(CH_3O)_2P^+$ (93)	80 20	13	14
$(CH_3O)_3PSH^+$ + $(CH_3O)_3P$	$(CH_3O)_3PH^+$ (125)	100	10	14

[a] Primary product distribution, ions of ≥10% abundance. [b] k in units of $\times 10^{-10}$ cm^3 molecules^{-1} s^{-1}. [c] Calculated using ref 25.

situated outside the collision chamber. All the spectra were signal averaged (≥10 spectra) at scan rates of ca. 90 s/scan. Another instrument used in these experiments is a virtual image, double focussing mass spectrometer with the EB geometry (Jeol JMS-D300/JMA-3500). A 3-keV collision energy and helium target gas were used in the collision-activated dissociation experiments (B/E linked scans[12]). Different parent ion beam attenuations did not have significant effects on the data; the data shown utilized 30–50% attenuation.

Low-energy collision-activated dissociation was carried out using two different instruments. A triple quadrupole mass spectrometer (a Finnigan-MAT TSQ 4500) was set to perform daughter scans.[13] Argon was used as the collision target in the center quadrupole at different nominal pressures (read by a Hastings thermocouple gauge directly connected to the quadrupole collision chamber); less than 0.1 mTorr was used for single-collision conditions,[14] 2 mTorr for multiple collision conditions. All the spectra shown were obtained using single-collision conditions unless otherwise specified. All the spectra are signal averaged (≥10 spectra).

The majority of the work, including all the ion–molecule reaction studies (Table III), was carried out on a Fourier-transform ion cyclotron resonance (FT-ICR) instrument, a prototype dual-cell Extrel FTMS 2001 mass spectrometer[15] with a 2.8 T superconducting magnet. All the trapping plates were kept at 2 V. All the spectra shown are an average of at least 100 spectra acquired at a digitizer rate of 5.3 MHz, and using an excitation sweep with 2.7 MHz bandwidth, 3.2 kHz/μs sweep rate, and 105 V amplitude. The spectra were recorded as 32k data points subjected to one zero fill before Fourier transformation.

The base pressure in both sides of the cell is less that 1×10^{-9} Torr, and it is maintained with two turbomolecular pumps (Balzars TPU 330). Nominal reagent gas pressures were $(0.3-2) \times 10^{-7}$ Torr, as measured with two ionization gauges. The ionization gauges were calibrated using common procedures,[16] on the basis of several well-characterized reactions with known rates (e.g., reaction of $H_2S^{\bullet+}$ with H_2S; reaction of $C_2H_7O^+$ with ethanol).[17] These and other reference systems (e.g., reaction of $O_2^{\bullet+}$ with CH_4,[17] reaction of $C_2H_3O^+$ with acetone,[17] reaction of the fragment ion m/z 99 from triethyl phosphate with neutral triethyl phosphate[18]) were also used to verify that the experiments used in this work, involving transfer of the reactant ion from one side of the dual cell into the other side before rate measurement, give correct rate constants. The greatest error in the rate measurements arises from inaccuracy in estimating the pressure of the neutral reagent.[16b] The precision of the rate constants is better than ±5%; the accuracy is estimated to be better than ±50%.

Ions were collisionally cooled by using long time delays (1–6 s) immediately after transfer from one cell to another. In a few experiments, a high momentary pressure of argon was created by using pulsed gas introduction; this results in more efficient collisional cooling. Collisionally activated dissociation with argon (nominal pressure 1×10^{-7} Torr) was carried out for isolated ions after transfer into the other side of the dual cell. An excitation pulse with a fixed amplitude (0.08 V_{p-p}) and a variable duration (≤1 ms) was applied, followed by a fixed reaction time (≥50 ms). The laboratory ion kinetic energy after single-frequency on-resonance excitation in a cubic trap was recently demonstrated[19] to be 0.5 of that computed using the infinite parallel plate approximation, $E_{\mathrm{ion}} = q^2V^2t^2/8md^2$, where q is the ionic charge, V is the amplitude of the radio frequency excitation pulse, t is the radio frequency pulse duration, m is the ionic mass, and d is the distance between the excitation plates (4.7 cm). All ion kinetic energies reported in this paper were obtained using this correction. An ion of m/z 140 activated by 5–25 eV (laboratory frame) collisions with argon at a nominal pressure of 1×10^{-7} Torr is calculated (using the kinetic theory of gases) to undergo an average of 1–3 collisions within 50 ms, and 3–6 collisions within 100 ms; however, these two reaction times produced identical spectra. Reaction time of 100 ms is referred to as near-single-collision conditions and 500 ms as multiple-collision conditions (6–14 elastic collisions for the ion specified above).

Results

The fragmentation characteristics of the radical cations of several phosphorus esters were studied by subjecting them to high-energy collisional activation in two different sector mass spectrometers (collision energies in the keV range) and to low-energy collisional activation in a triple quadrupole mass spectrometer and in a Fourier-transform ion cyclotron resonance mass spectrometer (collision energies in the eV range).[14,20–23] All these MS/MS experiments yield a set of fragment ions which can be used to examine the structure of the activated, fragmenting precursor ion. Figures 1–4 and Table II summarize the most important results obtained for the phosphorus ester radical cations, protonated phosphorus esters, and selected fragment ions. Distonic reference ions were generated by dissociative ionization of suitable neutral precursors and subjected to collision-activated dissociation (Table II). These reference ions include an isomer of the radical cation of trimethyl phosphate, generated by dissociative ionization of dimethyl propyl phosphate (see Scheme IV later in this paper), and an isomer of ionized triethyl phosphate generated from two different sources: diethyl pentyl phosphate and diethyl methoxyethyl phosphate (see Scheme V later in this paper).

A variety of experimental conditions were used in the low-energy collision-activated dissociation experiments since these experiments are known to be sensitive to different experimental parameters.[20,21] For example, the time used for collisional activation of the kinetically excited radical cation of triethyl phosphate in the Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer was varied from 5 to 2000 ms at several collision energies (10–100 eV); this results in a differing number of activating collisions. At relatively short reaction times (50 – 100 ms, nominal pressure of argon 1×10^{-7} torr), the collision-activated dissociation spectra obtained using this instrument resemble closely those obtained at very low pressures (single-collision conditions) in the triple quadrupole mass spectrometer (Table II). Most of the FT-ICR and triple quadrupole data illustrated were obtained using these conditions wherein the majority of the ions undergo only one activating collision (see the Experimental Section). While the most informative experiments involved relatively high collision energies (>20 eV in the laboratory frame) and a small number

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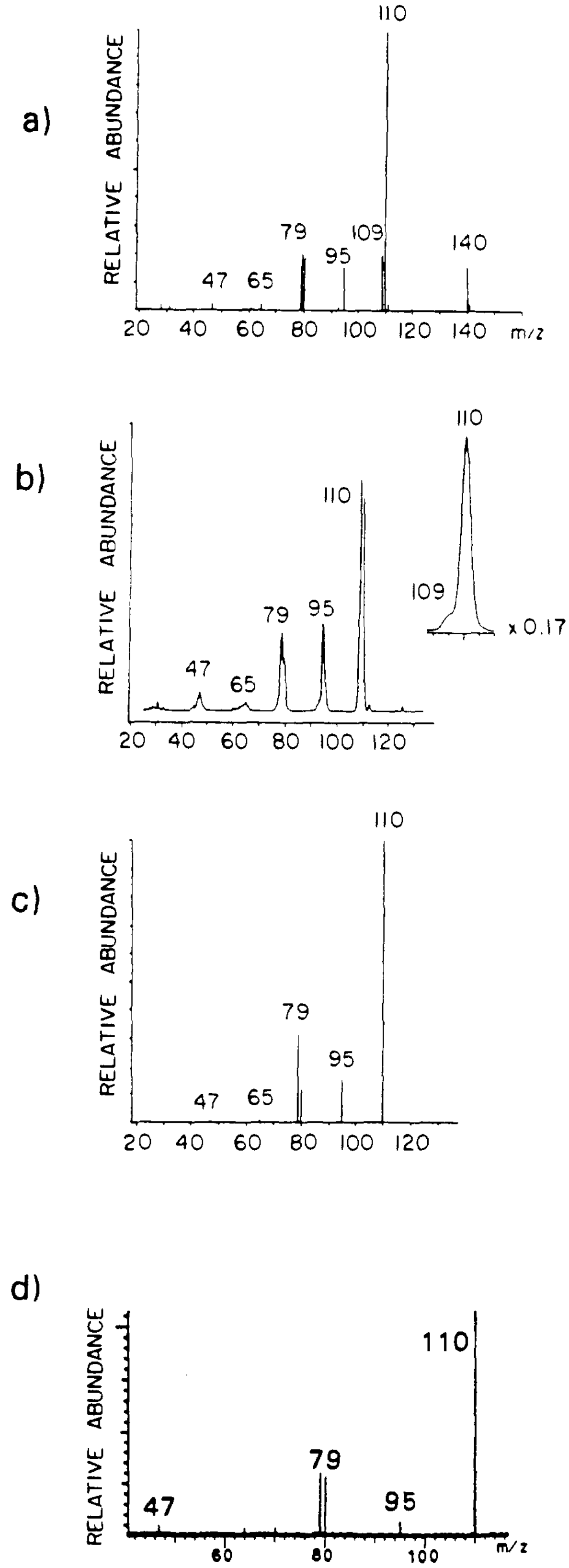


Figure 1. (a) 70-eV electron ionization mass spectrum of trimethyl phosphate. (b) High-energy (7 keV) collision-activated dissociation spectrum of the molecular ion of trimethyl phosphate. (c) Low-energy collision-activated dissociation spectrum of the molecular ion of trimethyl phosphate at 28 eV laboratory collision energy in the triple quadrupole instrument and (d) at 25 eV laboratory collision energy (50 ms reaction time) in the FT-ICR instrument. The fragmenting ion (*m*/*z* 140) is not shown in the collision-activated dissociation spectra.

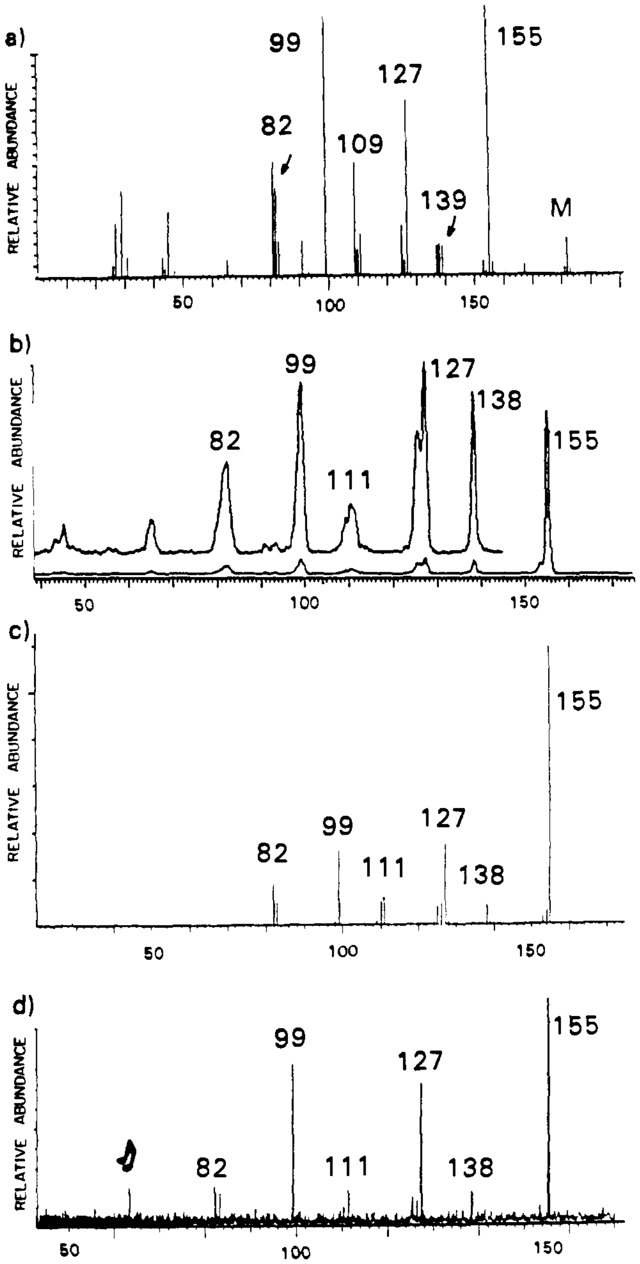


Figure 2. (a) 70-eV electron ionization mass spectrum of triethyl phosphate. (b) High-energy (7 keV) collision-activated dissociation spectrum of the molecular ion of triethyl phosphate. (c) Low-energy collision-activated dissociation spectrum of the molecular ion of triethyl phosphate at 28 eV laboratory collision energy in the triple quadrupole instrument and (d) at 25 eV laboratory collision energy in the FT-ICR instrument. The fragmenting ion (*m*/*z* 182) is not shown in the collision-activated dissociation spectra. The musical note symbol indicates interference caused by a local radio station.

of activating collisions, similar fragmentation pathways were accessed under multiple-collision conditions.

Ion isolation prior to collision-activated dissociation required special attention in all the different instruments used. In some cases, ions with a mass value within a mass unit of that of the radical cations of interest yielded fragment ions whose presence or absence proved to be crucial for the determination of the structure of the radical cations of interest (e.g., protonated trimethyl phosphate of *m*/*z* 141 produces, as its only major collision-activated dissociation product, the ion of *m*/*z* 109; see discussion for the importance of this fragment ion in structural characterization of the radical cation of trimethyl phosphate of *m*/*z* 140). The data illustrated are free of these interferences, with the possible exception of the high-energy collision-activated dissociation spectra; see discussion below. In the FT-ICR instrument, separation of ion generation and the following reactions

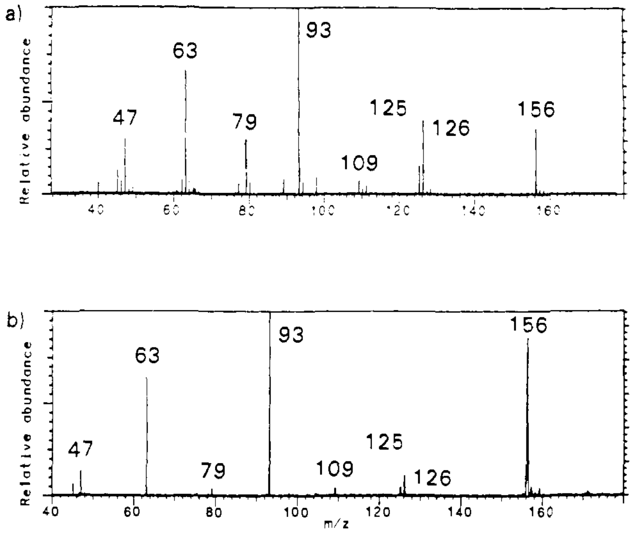


Figure 3. (a) 70-eV electron ionization mass spectrum of trimethyl phosphorothionate. (b) Low-energy collision-activated dissociation spectrum (50 eV, 500 ms reaction time) of the molecular ion of trimethyl phosphorothionate in the FT-ICR instrument. The molecular ion (*m/z* 156) was generated by 15 eV electron ionization.

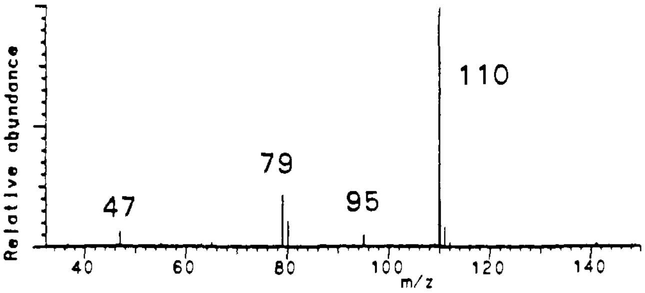


Figure 4. Low-energy collision-activated dissociation spectrum (50 eV, 100 ms reaction time) of the fragment ion of *m/z* 110 of trimethyl phosphate in the FT-ICR instrument.

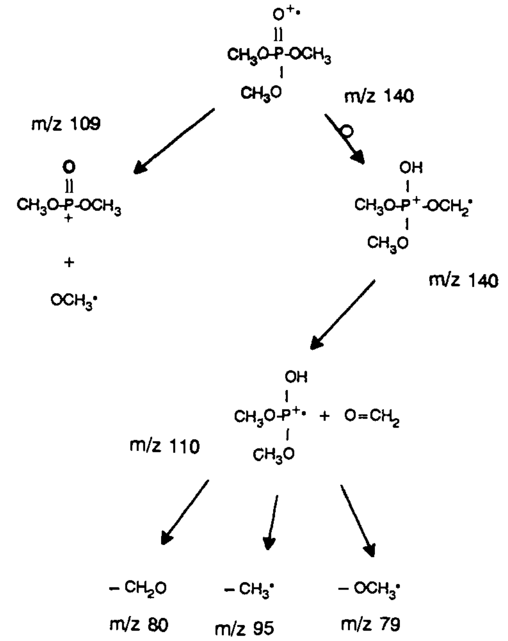
into different regions of the dual cell[24] proved to be essential since the radical cations of interest react rapidly with their neutral precursors.

In addition to dissociation reactions, ion–molecule reactions of several ions were studied in the FT-ICR; the most important results are summarized in Table III and in Figures 5–7. The ionization energy (IE) of trimethyl phosphorothionate was estimated to be 8.5–8.7 eV by examining (Table III) the occurrence or non-occurrence of charge exchange between neutral trimethyl phosphorothionate and ionized furan (IE = 8.883 ± 0.003 eV;[8] 100% charge exchange at 0.5 efficiency, i.e., $k_{\mathrm{obsd}}/k_{\mathrm{ADO}}$[25] = 0.5), ionized 2-methyl-2-butene (IE = 8.68 ± 0.1 eV;[8] a small amount of charge exchange), ionized 4-chlorotoluene (IE = 8.69 ± 0.02 eV;[8] 100% charge exchange at 0.8 efficiency), and ionized trimethyl phosphite (IE ≈ 8.5 eV; no reactions observed even at very long reaction times). The reverse reactions, ionization of neutral furan or neutral 4-chlorotoluene with ionized trimethyl thiophosphate, do not take place. However, ionized trimethyl phosphorothionate undergoes relatively fast charge exchange with neutral trimethyl phosphite (near 100% efficiency; see Table III and Figure 7).

Discussion

Differences between the electron ionization mass spectrum of a compound and the collision-activated dissociation spectra measured for the radical cation of this compound may indicate[7b,e] that the fragmenting ion structure is not the same in these experiments, especially if the observations cannot be explained on the basis of dissimilar amounts of internal excitation[26] in the ions. For simple organophosphorus compounds, the major features of the low-energy (≤20 eV) electron ionization mass spectra resemble those of the collision-activated dissociation spectra of the radical cations. However, there are *qualitative* differences between these two data sets for simple phosphates that are not instrument dependent, and that strongly suggest that the radical cations have isomerized prior to collision-activated dissociation. A detailed investigation of the bimolecular reactions of the organophosphate radical cations proves this to be true. In the following, a few of the systems studied are discussed in detail.

Scheme III



Trimethyl Phosphate: Dissociation Reactions. Electron ionization induced dissociation of trimethyl phosphate has been studied by several groups.[27] The lowest energy fragmentation[27] dominates dissociation of the radical cation of trimethyl phosphate. This reaction involves the loss of formaldehyde[27] and yields the radical cation of dimethyl phosphite (*m/z* 110).[23b] The ion of *m/z* 110 is the precursor to all the other fragment ions obtained for ionized trimethyl phosphate (Figures 1 and 4), with one important exception: the cleavage of a phosphorus–oxygen bond that results in the loss of a methoxy radical (fragment ion of *m/z* 109). Comparison of the electron ionization mass spectrum of trimethyl phosphate and the collision-activated dissociation spectra obtained for the corresponding radical cation reveals that while the loss of a methoxy radical is observed in the electron ionization experiments (Scheme III),[28] *it is not accessed upon low-energy collisional activation* (Figure 1). In the high-energy collision-activated dissociation experiments, a small amount of the ion of *m/z* 109 was observed; this, however, is probably the result of incomplete isolation of the molecular ion prior to collision-activated dissociation (see discussion in the Results section).

On the basis of energetic as well as kinetic considerations, the loss of a methoxy radical from ionized trimethyl phosphate should be observed in most of the low-energy collision-activated dissociation experiments since abundant product ions were generated from reactions that not only are slower (involve rearrangements) but also have higher energy requirements. For example, the formation of the ions of *m/z* 79 and 47 requires that several bonds be broken, and both processes involve rearrangement reactions (see Scheme III for formation of *m/z* 79). These reactions have

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(24) Laude, D. A., Jr.; Johlman, C. L.; Brown, R. S.; Weil, D. A.; Wilkins, C. L. *Mass Spectrom. Rev.* **1986**, *5*, 107.

(25) (a) Chesnavich, W. J.; Su, T.; Bowers, M. *J. Chem. Phys.* **1980**, *72*, 2641. (b) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.

(26) Wysocki, V. H.; Kenttämaa, H. I.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1987**, *75*, 181.

(27) (a) Bafus, D. A.; Gallegos, E. J.; Kiser, R. W. *J. Phys. Chem.* **1966**, *70*, 2614. (b) Santoro, E. *Org. Mass Spectrom.* **1973**, *7*, 589.

(28) Caserio, M. C.; Kim, J. K. *Adv. Chem.* **1985**, *215*, 65.

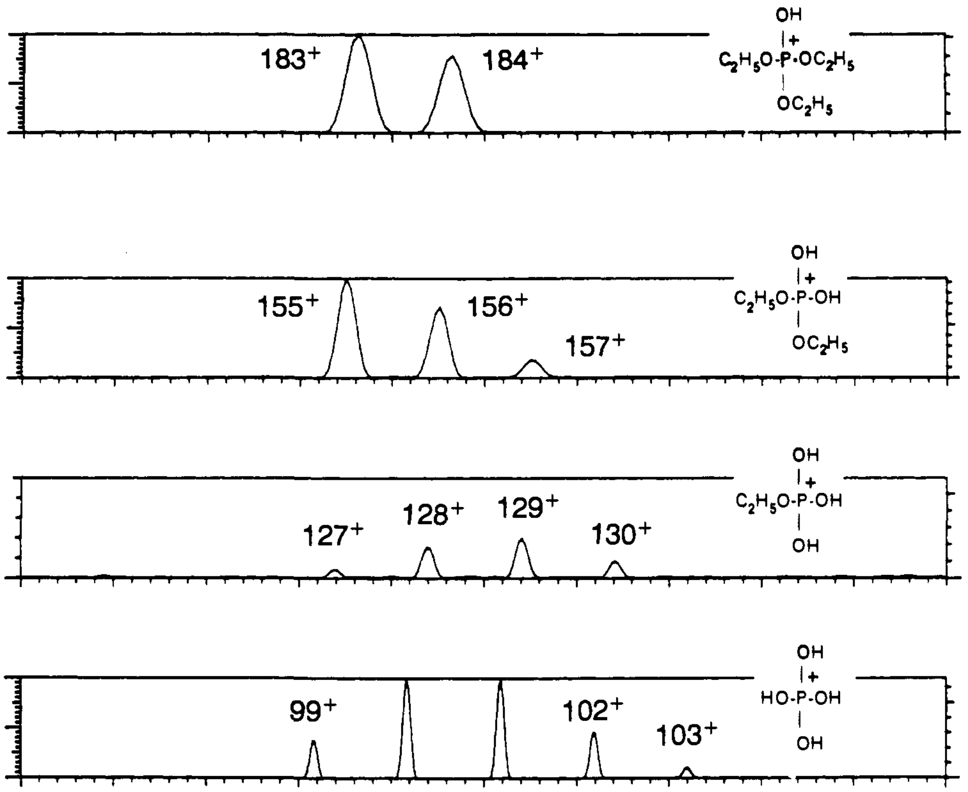


Figure 5. Thermoneutral hydrogen/deuterium exchange in phosphonium ions upon collisions with ND_3 in the FT-ICR instrument: (a) protonated triethyl phosphate (*m/z* 183); (b) the fragment ion of triethyl phosphate of *m/z* 155; (c) the fragment ion of triethyl phosphate of *m/z* 127; (d) the fragment ion of triethyl phosphate of *m/z* 99 (D_2O was used instead of ND_3).

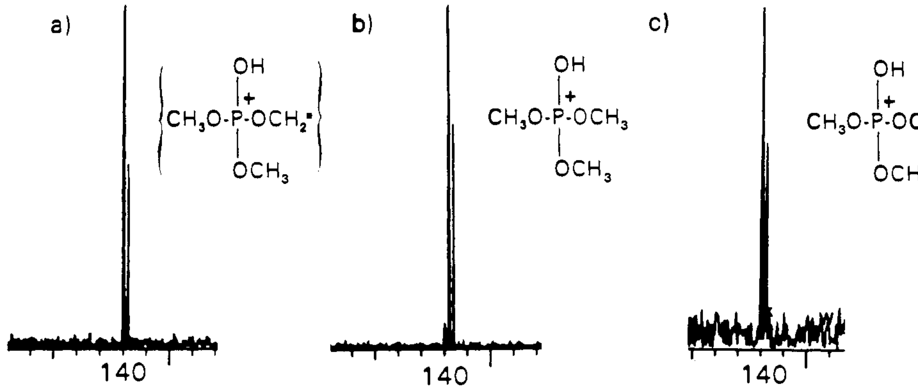
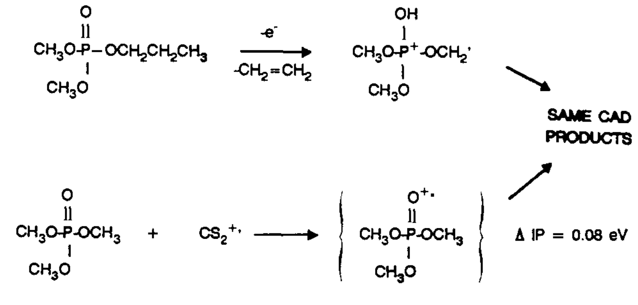


Figure 6. Thermoneutral hydrogen/deuterium exchange upon collisions with ND_3 in the FT-ICR instrument for (a) the molecular ion of trimethyl phosphate (*m/z* 140), (b) protonated trimethyl phosphate (*m/z* 141), and (c) a distonic reference ion (*m/z* 140) generated from dimethyl propyl phosphate.

estimated activation energies of 4.3 and 9 eV, respectively,[10] while electron ionization appearance energy measurements[10] indicate that the energy required for the loss of a methoxy radical is only 3.3 eV. Thus, in the experiments where the ions of *m/z* 47 and 79 are generated, the internal energy added to the radical cation *must be in excess* to that necessary for the methoxy loss to occur. Nevertheless, the reaction does not take place. This observation strongly suggests that one is dealing with different fragmenting ion structures in the electron ionization and in the collision-activated dissociation experiment.

It is quite conceivable that the dominant dissociation reaction of the radical cation of trimethyl phosphate (loss of formaldehyde) occurs in a stepwise manner as indicated in Scheme III and involves an intermediate distonic structure. If this ion represents a minimum on the potential energy surface, then some of the nonfragmenting ions sampled in the collision-activated dissociation experiments may have this distonic structure. This ion is not expected to readily lose a methoxy radical since the reaction not only involves a rearrangement but also has relatively high energy requirements when compared to other possible reactions. The most likely fragmentation for the distonic ion is a fast direct bond cleavage leading to loss of formaldehyde, and this indeed is the reaction that dominates the fragmentation of ionized trimethyl phosphate upon collisional activation.

Scheme IV



In order to investigate whether the long-lived radical cations of trimethyl phosphate have the distonic structure, a distonic reference ion was generated by dissociative ionization of dimethyl

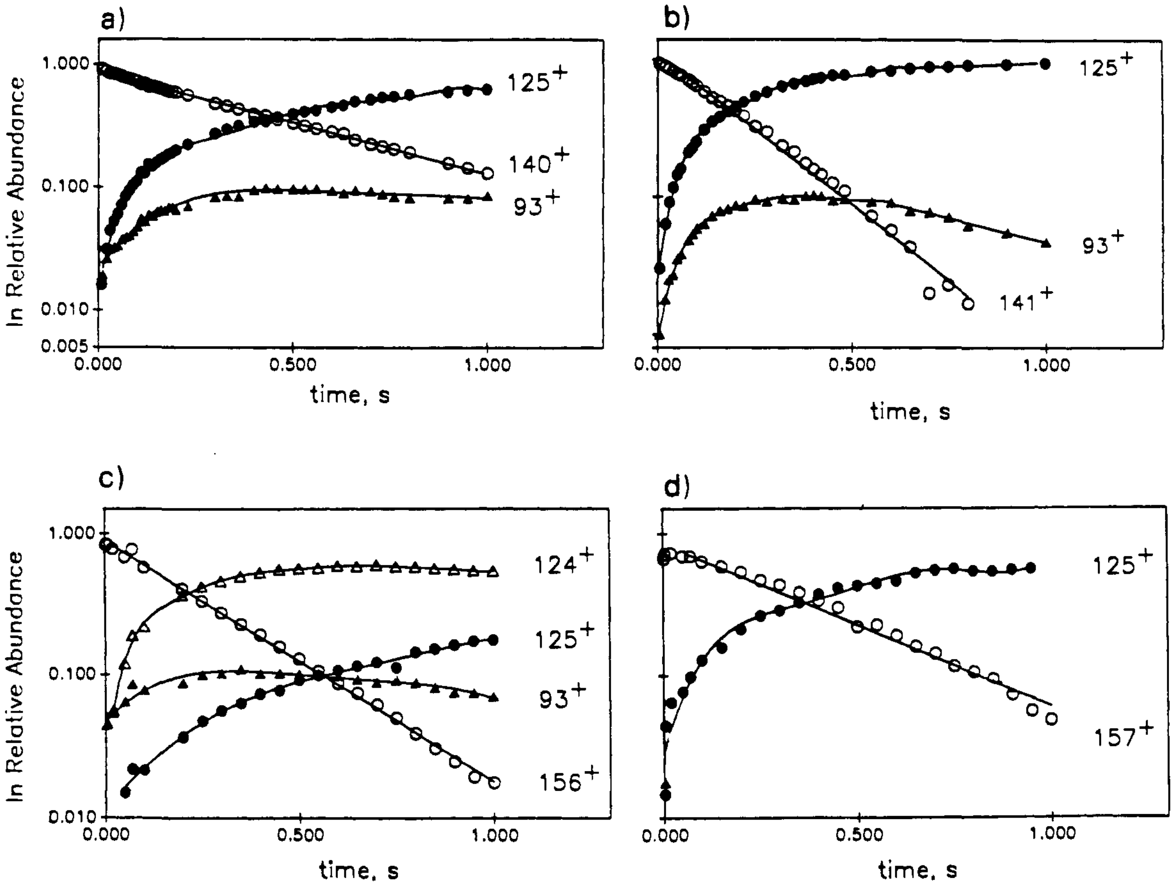


Figure 7. Formation of the most abundant product ions as a function of time in reactions of neutral trimethyl phosphite with (a) the molecular ion of trimethyl phosphate (*m/z* 140), (b) protonated trimethyl phosphate (*m/z* 141), (c) the molecular ion of trimethyl phosphorothionate (*m/z* 156), and (d) protonated trimethyl phosphorothionate (*m/z* 157). The nominal pressure of trimethyl phosphite was 4.6 × 10^{-7} Torr.

propyl phosphate (Scheme IV). Upon collisional activation, this ion was found to yield the same fragment ions with similar abundances and energy requirements as the long-lived radical cation of trimethyl phosphate (Table II). It is concluded that at some point during the experiment, the radical cation and the distonic reference ion must have the same structure or mixture of structures.

In order to minimize the amount of possible isomerization, the radical cation of trimethyl phosphate was generated with as little internal excitation as possible by charge exchange with $CS_2^{\cdot+}$ in the FT-ICR instrument. A maximum of 2 kcal/mol is deposited in trimethyl phosphate radical cation in this experiment if the charge exchange is a ground-state reaction, approximating the recombination energy of $CS_2^{\cdot+}$ with the ionization energy of CS_2 (10.07 eV;[8] electronically excited $CS_2^{\cdot+}$ is not expected to generate a stable radical cation of trimethyl phosphate: $\Delta H_{rxn} \approx -2.5$ eV;[10] fragmentation threshold ≈ 1 eV).[27a] Indeed, $CS_2^{\cdot+}$ charge exchange proved to be an efficient method to generate large amounts of stable trimethyl phosphate radical cations. Collision-activated dissociation of these ions produced spectra identical to those obtained for the ions generated by electron ionization (Table II). Collisional cooling of the molecular ions with argon at a nominal pressure of 1 × 10^{-7} Torr for as long as 6 s (more than 20 collisions) before collision-activated dissociation in the FT-ICR did not affect the dissociation product distribution. All these collision-activated dissociation spectra, while being similar to each other, are different from the electron ionization spectrum of trimethyl phosphate in one important way: no fragment ion of *m/z* 109 is observed in any of the collision-activated dissociation experiments. All these results support the proposal that the radical cation of trimethyl phosphate has isomerized to a distonic structure.

The results obtained are summarized in the potential energy surface shown in Figure 9. If the isomerization of the trimethyl phosphate radical cation occurs prior to collisional activation, as proposed above, its activation energy must be low since generation of the ions by a thermoneutral charge exchange reaction does not prevent this isomerization. The isomerization is estimated to be exothermic by more than 23 kcal/mol (see Scheme I for the approximation used in this estimate; it is assumed that the homolytic C–H bond energy in protonated trimethyl phosphate is similar to that of the α-C–H bond in protonated methanol and the β-C–H bond in protonated ethanol, i.e., 103–106 kcal/mol[6]). The lowest energy fragment ion of *m/z* 110 yields most of the collision-activated dissociation products of the ionized trimethyl phosphate/distonic ion system. Note that this finding contrasts with the earlier suggestions concerning the fragmentation pathways of ionized trimethyl phosphate: the fragment ions of *m/z* 79 and 47 were proposed[27] to arise via the fragment ion of *m/z* 109.

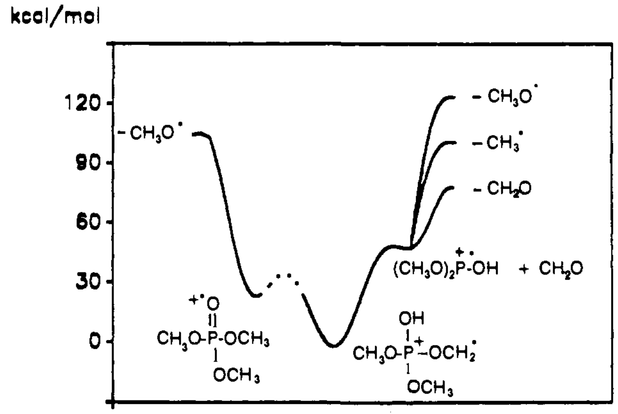


Figure 8. Potential energy surface for the isomerization and dissociation of the molecular ion of trimethyl phosphate.

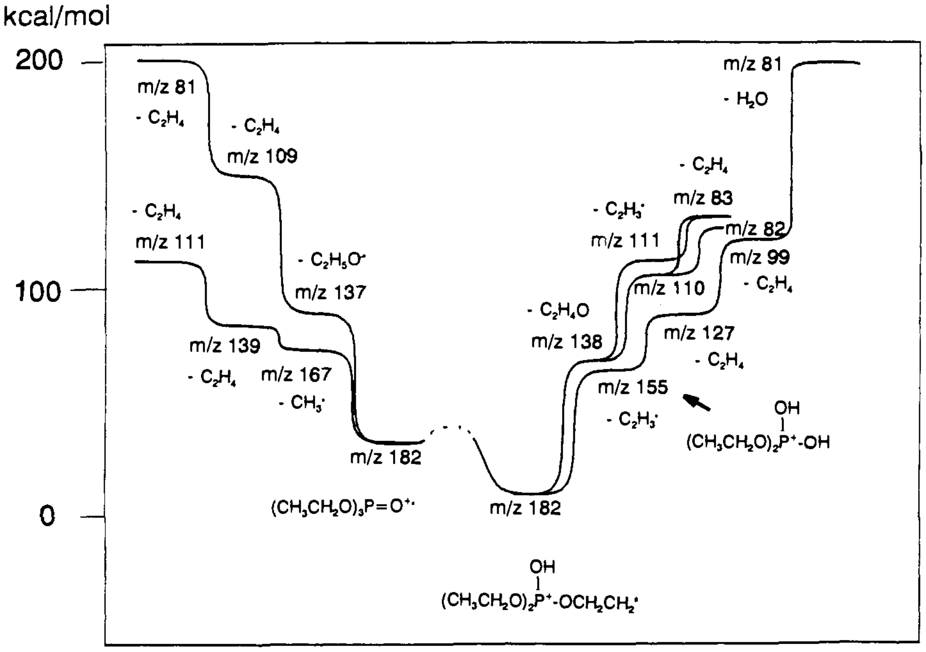


Figure 9. Potential energy surface for the isomerization and dissociation of the molecular ion of triethyl phosphate. Only well-characterized[14,26] ion structures and established[14,26] fragmentation pathways are shown, with one exception: the formation of the ion of *m/z* 109 from *m/z* 137 has been assumed.[26a] For the structures of the ions of *m/z* 127, 99, and 81, see refs 26 and 30. Note: two different ions of *m/z* 111 are generated.[14,26a] The same threshold is indicated for both, and this should be considered as the lower limit.

The observation of an abundant fragment ion of *m/z* 109 upon electron ionization of trimethyl phosphate is explained by the fact that only fast fragmentations are observed in this experiment (typically occurring within a few microseconds after ionization). Fast direct bond cleavages (i.e., formation of 109^+) can compete efficiently with the energetically favored but slower isomerization in the highly excited ions that fragment within a few microseconds. Hence, the spectra obtained by electron ionization reflect fragmentation of a mixture of the original and the rearranged forms of the radical cation. The only dissociation reaction accessible to the original, unrearranged ion (the loss of a methoxy radical; loss of $H^\bullet$ has been discussed[27] before but was not observed in the experiments discussed here) is absent in the collision-activated dissociation spectra due to isomerization of the long-lived ions during the experiment. It is conceivable, however, that this isomerization is *caused* by the collisional activation process. In order to examine this possibility, bimolecular reactions of the long-lived radical cations were examined in the FT-ICR.

Trimethyl Phosphate: Ion–Molecule Reactions. Most gaseous distonic ions studied thus far can be considered as protonated radicals.[1] This also applies to the distonic isomer of the trimethyl phosphate radical cation. Thus, this distonic ion may be expected to behave like the corresponding even-electron ions, protonated phosphates or phosphonium ions, when allowed to react with basic neutral reagents.

The bimolecular reactions of the trimethyl phosphate radical cation were compared to those of various reference phosphonium ions. Examination of thermoneutral hydrogen/deuterium exchange reactions of these ions with suitable deuterated reagents,[29] such as deuterated ammonia (deuterium at the basic site; proton affinity somewhat below the proton affinity of the conjugate base of the phosphorus ion of interest), demonstrated that the number of H/D exchanges reflects the number of hydroxyl groups present in the phosphonium ions (Figure 5). Deuterated ammonia appears to be useful also when examining the structures of *radical cations*. The fragment ion of *m/z* 110 generated from trimethyl phosphate has one hydroxyl group[14] (see Scheme III), and it undergoes one hydrogen/deuterium exchange upon collisions with this reagent. Therefore, thermoneutral H/D exchange reactions may allow distinction between the conventional and distonic isomers of the radical cation of trimethyl phosphate. The former structure is not expected to readily undergo H/D exchange since it does not have acidic functional groups at the charge site; however, if exchange involving the methyl groups can take place, nine consecutive exchanges are expected (assuming that the ion does not rearrange during the experiment). A more likely reaction, however, is abstraction of a deuterium atom, estimated to be exothermic by about 20 kcal/mol for deuterated ammonia.[8]

In sharp contrast to the expectations discussed above, the radical cation of trimethyl phosphate was observed to *exchange one hydrogen atom with deuterium* (Figure 7) at approximately the same rate as this exchange takes place for protonated trimethyl phosphate. Reaction of the distonic reference ion also results in exchange of one hydrogen atom with deuterium. These results indicate that (1) the long-lived radical cation of trimethyl phosphate contains one exchangeable hydrogen atom, (2) this hydrogen atom is likely to be in a similar environment as the hydroxyl proton in protonated trimethyl phosphate (similar reaction rate), and (3) the distonic reference ion is not in equilibrium with the conventional isomer since this would result in exchange of more than one hydrogen atom with deuterium.

Further support for the proposed distonic structure for the long-lived, low-energy radical cation of trimethyl phosphate was obtained from examination of the reaction of this ion with neutral trialkyl phosphites (Table III). Trimethyl phosphite is expected to readily donate an electron to the radical cation of trimethyl phosphate if this ion has the original structure since the reaction would be exothermic by 34 kcal/mol (Table I). On the other hand, trimethyl phosphite is a strong base, and it is able to deprotonate most protonated organophosphates, including protonated trimethyl phosphate (deprotonation is exothermic by 9 kcal/mol; Table I). In spite of the great exothermicity of the possible charge exchange reaction, the radical cation of trimethyl phosphate was found to predominantly protonate neutral trimethyl phosphite (Table III). This proton transfer can be followed by decomposition of the protonated trimethyl phosphite (*m/z* 125) by loss of methanol to give an ion of *m/z* 93 (Figure 7). Other trialkyl phosphite reagents were also studied. Upon collisions with neutral triethyl

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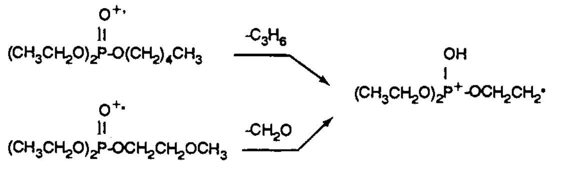
[29] (a) Squires, R. R.; Bierbaum, V. M.; Grabowski, J.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 5185. (b) Squires, R. R.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 4256. (c) Ausloos, P.; Lias, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 3641. (d) Hunt, D. F.; Sethi, S. *J. Am. Chem. Soc.* **1980**, *102*, 6953.

Scheme V



phosphite and with neutral triisopropyl phosphite, the radical cation of trimethyl phosphate yields proton transfer products that consist of more than 90% of the primary products. This occurs in spite of the fact that electron transfer to the original structure of the radical cation of trimethyl phosphate would be exothermic by 37 kcal/mol for triethyl phosphite and 39 kcal/mol for triisopropyl phosphite.

Triethyl Phosphate. Results from experiments on the radical cation of triethyl phosphate suggest that this species also rapidly isomerizes to one or several stable distonic structures even when generated with only small amounts of internal energy. This ion has only one major fragmentation pathway[27a,30] (Figure 1): loss of $C_2H_3^{\bullet}$ followed by consecutive losses of the remaining two ethyl groups as ethylenes (formation of *m*/*z* 155, 127, and 99), and finally water (formation of *m*/*z* 81). Another fragmentation pathway begins with the loss of acetaldehyde, followed by two consecutive losses of two carbon units as $C_2H_3^{\bullet}$ or C_2H_4 (formation of *m*/*z* 138, 111, 110, 83, and 82). Both of these pathways are accessed in all of the experiments discussed here. Figure 9 shows the energetics associated with the formation of the major fragment ions of the radical cation of triethyl phosphate.

The main features of the electron ionization mass spectrum of triethyl phosphate are similar to those of the collision-activated dissociation spectra of the radical cation (Figure 2, Table II). However, a fragment ion (*m*/*z* 137) that arises from cleavage of a phosphorus–oxygen bond and loss of an ethoxy radical is only observed in the electron ionization mass spectrum, in spite of the fact that this reaction requires[10] less energy than, for example, formation of the ions of *m*/*z* 99, 110, 111, 83, and 82 (see Figure 9) that are all generated upon collisional activation of the radical cation. This finding is analogous to the observations concerning the methoxy radical loss from the radical cation of trimethyl phosphate. A careful examination of the electron ionization mass spectrum and the collision-activated dissociation spectra reveals that there are other fragmentation pathways, as well, that are energetically accessible in most of the collisional activation experiments but that are only observed upon dissociative ionization of triethyl phosphate. These include the formation of an ion of *m*/*z* 139 which, according to earlier studies,[27a] involves the loss of a methyl radical from the molecular ion, followed by the loss of ethylene. Another example is the formation of an ion of *m*/*z* 109, suggested[27a] to involve loss of ethylene from the ion of *m*/*z* 137. Note that all the reactions that are expected to occur upon collisional activation of the radical cation but that are not observed require *a direct bond cleavage in the unrearranged molecular ion.*

All the findings presented above suggest that an isomerization may have occurred for the long-lived radical cation of triethyl phosphate. In support of this proposal, similar fragmentation patterns are obtained for a distonic reference ion and for the radical cation of triethyl phosphate (Scheme V; Table II). Ionization of triethyl phosphate using $CS_2^{\bullet+}$ charge exchange ($\Delta H_{rxn} = -6$ kcal/mol) and by electron ionization results in identical collision-activated dissociation spectra (Table II). Thus, if the radical cation isomerizes after ionization and before collisional activation, the barrier for the isomerization must be low (below 6 kcal/mol). The isomerization is estimated to be exothermic by 23–26 kcal/mol (assuming a homolytic β-C–H bond energy of 103–106 kcal/mol[6] in protonated triethyl phosphate). The experimental results do not allow one to rule out hydrogen shifts between the ethyl groups in the resulting distonic ion. However, it is indicated that 1,6-hydrogen shifts do not lead to *abundant* isomerized structures. These hydrogen shifts would generate a new distonic isomer, $(CH_3CH_2O)_2P^+(OH)OCH^{\bullet}CH_3$, which is expected to readily lose CH_3CHO. While loss of CH_3CHO is observed (Figure 2), it does not lead to an abundant product ion (*m*/*z* 138) under any conditions investigated (Table II).

For dissociation of the radical cation of triethyl phosphate, energetically favored rearrangement reactions involving hydrogen transfer to the phosphoryl oxygen via a six-membered transition state compete efficiently with direct bond cleavages. Since rearrangement reactions dominate the dissociation even upon electron ionization, possible isomerization of the radical cation is very difficult to verify on the basis of dissociation reactions alone. However, examination of the ion–molecule reactions of the long-lived radical cation of triethyl phosphate shows conclusively that this ion has a distonic structure. Upon collisions with trimethyl phosphite, proton transfer rather than electron transfer dominates (Table III). This reactivity resembles that observed for protonated triethyl phosphate and for the distonic reference ion, and the rates of all these reactions are similar. Reaction of the radical cation with deuterated ammonia further substantiates this hypothesis: exchange of one hydrogen atom with deuterium, rather than deuterium atom abstraction, was observed. Protonated triethyl phosphate also exchanges one hydrogen atom with deuterium (Figure 5) when reacted with deuterated ammonia. All these findings are in analogy with those obtained for the ionized trimethyl phosphate/distonic ion system.

Trimethyl Phosphorothionate. The results obtained for the radical cation of the only thioester studied, trimethyl phosphorothionate, are quite different from those obtained for the ionized phosphates. The only fragmentation reaction expected to occur for the conventional, unrearranged radical cation is the loss of a methoxy radical to yield an ion of *m*/*z* 125.[30] This reaction is observed upon collisional activation of the radical cation, as well as upon electron ionization of trimethyl phosphorothionate (Table II; Figure 4). The loss of a methoxy radical was verified to occur *directly* from the radical cation and not via the fragment ion of *m*/*z* 126 formed by loss of formaldehyde; this ion produces most of the other dissociation products of the radical cation of trimethyl phosphorothionate (Table II). Although no activation energies are available for the dissociation reactions discussed, these findings strongly suggest that radical cations *with the original structure* fragment in the electron ionization experiment as well as in the collision-activated dissociation experiments. The major dissociation pathways of this radical cation are shown in Scheme VI.

The results obtained in the ion–molecule reaction studies conclusively show that only the original ion structure is generated by removal of an electron from trimethyl phosphorothionate. Reaction of the radical cation of trimethyl phosphorothionate with deuterated ammonia for as long as 6 s (over 30 collisions) gave no evidence of exchange of a hydrogen atom with deuterium. However, protonated trimethyl phosphorothionate undergoes one H/D exchange with deuterated ammonia under the same conditions. These data suggest that the radical cation of trimethyl phosphorothionate does not contain SH or OH groups at the charge site. Reaction of the radical cation with neutral trimethyl phosphite provides further support for this conclusion. Charge exchange between trimethyl phosphite and the radical cation of the original structure is nearly thermoneutral, while proton transfer from the possible distonic structure to trimethyl phosphite would be exothermic by about 6 kcal/mol (proton affinity of the conjugate base of the distonic ion is assumed to be similar to that of trimethyl phosphorothionate). In spite of the greatly favorable energetics for proton transfer, no primary products from this reaction were observed. The favored channel is charge exchange (production of *m*/*z* 124; Table III, Figure 8). For protonated trimethyl phosphorothionate, however, the primary product of the reaction with trimethyl phosphite arises from proton transfer (*m*/*z* 125).

On the basis of the published ionization energy for trimethyl phosphorothionate (≤9.16 eV[8]), the isomerization of the radical cation of trimethyl phosphorothionate to a distonic form is exothermic by 6–9 kcal/mol, and, in analogy with ionized trimethyl

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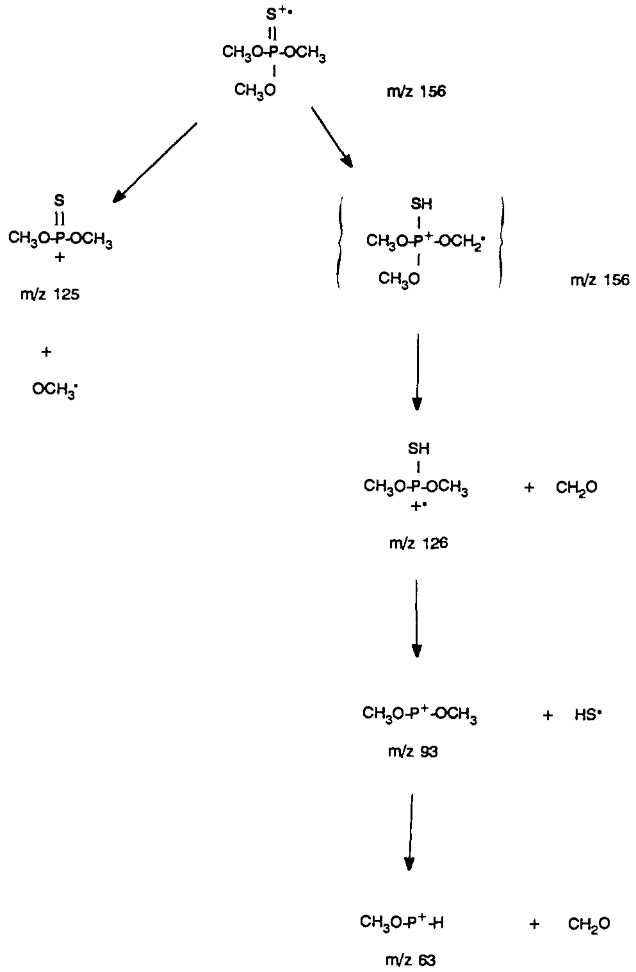
(30) Granoth, I. *Top. Phosph. Chem.* **1976**, *8*, 41.

Scheme VI



phosphate, it should take place. However, the ionization energy of trimethyl phosphorothionate was remeasured in this work to be 8.5–8.7 eV. On the basis of this ionization energy, the isomerization of the radical cation to a distonic structure is *endothermic* by 1–9 kcal/mol (estimated using 103–106 kcal/mol[6] for the homolytic C–H bond energy in protonated trimethyl phosphorothionate). This explains why no appreciable isomerization was observed for the radical cation.

Other Phosphorus Esters. The isomerization of the radical cations of phosphorus esters to distonic structures can be expected to be thermodynamically favored for all those compounds for which the hydrogen atom affinity (HA) is greater than 103–106 kcal/mol. This is true for simple organophosphates and phosphine oxides (Table I). Similar thioesters have significantly lower hydrogen atom affinities, and are therefore not expected to isomerize readily. This is supported by the results presented here for the radical cation of trimethyl phosphorothionate. On the basis of Table I, isomerization is not likely to be favored for trimethyl phosphite and trimethyl phosphine since their hydrogen atom affinities are equal to or lower than 103 kcal/mol. The results shown in Table II for the radical cation of trimethyl phosphite are in agreement with earlier findings,[7b,e] and suggest that no isomerization has taken place after ionization: upon collisional activation, these ions undergo a fast cleavage of a phosphorus–oxygen bond leading to loss of a methoxy radical (formation of the ion of m/z 109). Larger phosphites and phosphines, however, may be expected to isomerize after ionization (hydrogen affinities $\geq$105 kcal/mol). Indeed, the collision-activated dissociation data for the radical cation of triethyl phosphite suggest that these ions have isomerized: no ethoxy radical loss is observed for these ions upon collisional activation although this dissociation yields an abundant fragment ion (m/z 121; Table II) upon electron ionization of the neutral molecule. This finding is in analogy to those discussed earlier in this paper for the molecular ions of trimethyl phosphate and triethyl phosphate.

Conclusion

It is well established[1] that distonic ions are common intermediates in dissociation of isolated ions. This work demonstrates that the importance of distonic ion structures extends beyond the chemistry of internally excited ions: *the long-lived, low-energy radical cations of simple organic phosphates exist as their more stable distonic forms in the gas phase.* Furthermore, the existing evidence and thermochemical considerations suggest that the radical cations of long-chain organophosphonates,[7b,e] phosphites, phosphines, and phosphine oxides are also likely to isomerize in the gas phase.

The distonic ions studied here, as well as most gaseous distonic ions investigated thus far, can be considered as protonated radicals. These distonic ions behave like the related even-electron ions in reactions with basic molecules. Thermoneutral hydrogen/deuterium exchange reactions provide a powerful tool for identification of such ion structures since all their acidic hydrogen atoms are exchanged with deuterium atoms upon collisions with suitable deuterated reagent molecules, such as deuterated ammonia.

In contrast to the results obtained for organophosphates, ionized trimethyl phosphorothionate does not isomerize to a distonic structure. The ionization energy of trimethyl phosphorothionate, reported in the literature[8] to be $\leq$9.15 eV, was redetermined here to be 8.5–8.7 eV. On the basis of this revised ionization energy, the conventional structure of ionized trimethyl phosphorothionate is concluded to be more stable than the distonic form. The same is likely to be true for other phosphorus thioesters, as well. Therefore, the radical cations of phosphorus thioesters are expected to retain their original structure in the gas phase.

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