

Tautomer Characterization by Energy Resolved Mass Spectrometry. Dimethyl Phosphite and Dimethyl Phosphonate Ions

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Abstract: The formation, relative stability, isomerization, and fragmentation of the title tautomers are studied by tandem mass spectrometry. Collision-induced dissociation, when performed over a range of energies, yields breakdown curves which allow the phosphite and phosphonate structures to be distinguished. Thermochemical arguments show that the phosphite structure is significantly more stable. Isomerization occurs in competition with fragmentation; the isomerization barrier is estimated to be between 0.7 and 1.4 eV. Under multiple collision conditions, isomerization of the dimethyl phosphonate ion to the dimethyl phosphite ion is essentially complete. The increased tendency for isomerization which accompanies collisional activation under multiple collision conditions is a feature of this method in ion structure characterization. Isomerization also occurs preferentially for low-energy ions, so that single-step excitation to yield high-energy ions is the preferred procedure for tautomer differentiation. In contrast to the behavior of the methyl compounds, the corresponding ethyl analogues are almost indistinguishable by energy resolved mass spectrometry, even under single-collision conditions. In fragmentations of these phosphorus compounds, hydrogen rearranges to the PO group to generate the P-OH structure in preference to the P(O)H structure. This and several other findings are contrary to previous assumptions.

A long-standing controversy in solution phosphorus chemistry has concerned the structure of the simplest phosphorus oxy acids.^{1,2} Two tautomeric forms, a and b, can be considered for these



(a)

(b)

R = H, OH, alkyl, alkoxy

molecules. It is now well established^{1–3} that these structures are in equilibrium, and that the phosphoryl tautomer (b) predominates, presumably because of the very strong P=O bond. The less stable phosphite tautomer (a) has only once been isolated; bis(trifluoromethyl)phosphine oxide exists predominantly in this form.⁴ In addition, there is evidence that tautomer a is a reactive intermediate in several other cases.³ Very recently, pulsed ion cyclotron double resonance has been used to determine the relative thermochemical stabilities of dimethyl phosphonate and its tautomer, dimethyl phosphite, in the gas phase.² Dimethyl phosphite was prepared in the gas phase from protonated dimethyl phosphonate via proton abstraction with a strong base. Based on the relative proton affinities of the two tautomers, neutral dimethyl phosphonate was concluded to be 27 kJ/mol more stable than dimethyl phosphite.

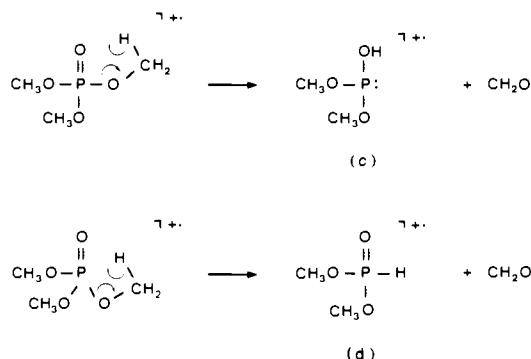
The relative stabilities of neutral phosphorus compounds have frequently been used as a guide to the stabilities of the corresponding ions.^{1,5,6} Therefore, the positively charged ions containing a P(O)H group have been assumed to be energetically more stable than their tautomers containing a trivalent phosphorus P-OH group, which, if formed at all, have been assumed to immediately isomerize to the phosphonate tautomers.^{1,5} For example, the ionic product of the dominant fragmentation reaction of ionized methyl phosphates (the loss of CH₂O accompanied by a hydrogen shift) has generally been assumed to have the phosphonate structure.⁶ Most fragmentations of positively charged phosphorus esters involve transfer of hydrogen to the heteroatom moiety.⁷ Nevertheless, no studies concerning either the site to which the hydrogen transfer actually occurs, or the possible subsequent isomerization of the fragment ion, have been reported. The need for such a study derives both from the intrinsic and practical importance of phosphorus esters^{3,8} and from the sig-

nificant role of mass spectrometry in their characterization as pesticides, drugs, and endogenous toxic agents.⁷ Immediate impetus derives from the fact that the relative stabilities of gas-phase ions do not necessarily correlate with those of gas-phase neutrals. For instance, enol radical cations are thermodynamically more stable than their keto tautomers by some 60–130 kJ/mol, and in many cases the isomers are stable toward interconversion.^{9,10} Furthermore, it has been suggested very recently that the enol form of the positively charged molecular ion of dimethyl methylphosphonate is more stable than the keto form.¹¹ In this work, the dimethyl methylphosphonate ion was shown to undergo slow keto-to-enol isomerization after ionization, the most striking consequence of this being that collision-induced dissociation of this ion totally failed to produce a characteristic fragment ion of the keto form (loss of CH₃⁺).

Differentiation of the tautomeric structures a and b of ionized dialkyl phosphonates is especially challenging since the structural distinction depends upon which of the neighboring atoms, phosphorus or oxygen, holds the hydrogen atom; i.e., only a 1,2-hydrogen shift is needed for isomerization. If isomers such as a and b can be differentiated, it should be possible to draw conclusions about the site to which the hydrogen transfer preferentially occurs in ionized phosphorus esters, and about which of the tautomeric structures is the preferred ionic form. Tandem mass spectrometry (MS/MS), and especially energy-resolved mass spectrometry, has proved to be an extremely useful method for structural studies of isomeric ions.^{10–13} This paper reports results obtained with

- (1) Haake, P.; Ossip, P. S. *Tetrahedron* **1968**, *24*, 565.
- (2) Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 3594.
- (3) Emsley, J.; Hall, D. "The Chemistry of Phosphorus"; Harper & Row Ltd.: London, 1976.
- (4) Griffiths, J. E.; Burg, A. B. *J. Am. Chem. Soc.* **1960**, *82*, 1507.
- (5) Griffiths, W.; Tebby, J. C. *Phosphorus Sulfur* **1978**, *5*, 101.
- (6) Santoro, E. *Org. Mass Spectrom.* **1973**, *7*, 589.
- (7) Reviews: (a) Gillis, R. G.; Occoclowitz, J. L. "The Mass Spectrometry of Phosphorus Compounds" in "Analytical Chemistry of Phosphorus Compounds", Halmann, M., Ed.; Wiley-Interscience: New York, 1972. (b) Chapman, J. R. *Organophosphorus Chem.* **1983**, *14*, 278. (c) Granath, J. *Top. Phosphorus Chem.* **1976**, *8*, 41.
- (8) Eto, M. "Organophosphorus Pesticides: Organic and Biological Chemistry"; CRC Press: Cleveland, Ohio, 1974.
- (9) Levens, K.; Schwartz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77.
- (10) "Tandem Mass Spectrometry"; McLafferty, F. W., Ed.; Wiley-Interscience: New York, 1983.
- (11) Holtzclaw, J. R.; Campana, J. E., 31st Annual Conference on Mass Spectrometry and Allied Topics, Boston, Mass. 1983; p 312.
- (12) Verma, S.; Ciupak, C. D.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Proc.*, in press.

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Scheme I

various MS/MS methods concerning the formation, relative stability, isomerization, and fragmentation of the tautomers of ionized dialkyl phosphonates.

Experimental Section

High-energy collision-induced dissociation (CID) experiments were performed with a reversed geometry sector instrument of the MIKES (mass-analyzed ion kinetic energy spectrometer) type.¹⁴ Electron impact ionization (200-eV electron energy) was used to generate the ions. Ion kinetic energy (collision energy) was 7 keV. Air at a nominal 3×10^{-5} torr pressure was used as the collision target; this pressure corresponds approximately to single collision conditions. Low-energy collision-induced dissociation, as well as energy-resolved mass spectrometry,¹⁰ was done with a Finnigan triple quadrupole mass spectrometer.¹⁵ The ions were generated by electron impact ionization (70-eV electron energy). Argon was used as the collision target. Breakdown graphs were measured by gradually increasing the collision energy from about 5 to 28 eV and recording daughter spectra at each energy. Collision gas pressure was varied from about 0.2 mtorr (corresponding to single collision conditions) to 2 mtorr (corresponding to multiple collision conditions). The data are not corrected for metastable peaks. All compounds were purchased from Alfa and were used without further purification.

Results and Discussion

Two different MS/MS techniques were used to study dimethyl phosphonate and two of its isomers, and diethyl phosphonate and its phosphite tautomer. Mass-selected ions were subjected to high-energy collisional activation in a MIKES instrument,¹⁰ and to low-energy collisional activation in a triple quadrupole mass spectrometer.^{10,15} Both experiments yield a set of fragment ions which can be represented as the daughter spectrum of the selected ion. The low-energy method is particularly sensitive to several variables, including collision energy, collision target pressure, and the nature of the collision target. Changes in these parameters change the energy deposited in the selected ion and hence its fragmentation pattern as exhibited in the MS/MS spectrum.¹⁶ A difference in the initial internal energy of the ions prior to excitation contributes differences to the MS/MS spectrum and may make structural distinctions difficult when closely related ion structures are compared,¹⁷ as in this study. In these cases, measurement of the mass spectra at several internal energies of the fragmenting ions, i.e., the energy-resolved mass spectrometry experiment,¹⁰ is a useful adjunct to the usual methods of collisional activation. With a triple quadrupole mass spectrometer, a systematic examination of the dependence of fragmentation patterns on the internal energy of the fragmenting ion (construction of a breakdown graph) is best done by systematically changing the collision energy. The results obtained by changing the other variables mentioned above are sometimes more difficult to interpret unambiguously.¹⁰

(13) Fetterolf, D. D.; Yost, R. A. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *44*, 37.

(14) Beynon, J. H.; Cooks, R. G.; Amy, J. W.; Baitinger, W. E.; Ridley, T. Y. *Anal. Chem.* **1973**, *45*, 1023A.

(15) Slayback, J. R. B.; Story, M. S. *Ind. Res. Dev.* **1981** (Feb), 129–139.

(16) Kenttämaa, H. I.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Proc.*, in press.

(17) Levensen, K. "Fundamental Aspects of Organic Mass Spectrometry"; Verlag Chemie, New York, 1978.

Table I. High-Energy CID Spectra for the $[M - CH_2O]^{+}$ Ion of Trimethyl Phosphate (c) and the Molecular Ion of Dimethyl Phosphonate (d)

<i>m/z</i>	relative abundance (%) ^a	
	c	d
95	35	27
93	4	4
80	63	162
79	100	100
65	6	8
47	20	16
31	4	9

^a Normalized to *m/z* 79 for purposes of comparison.

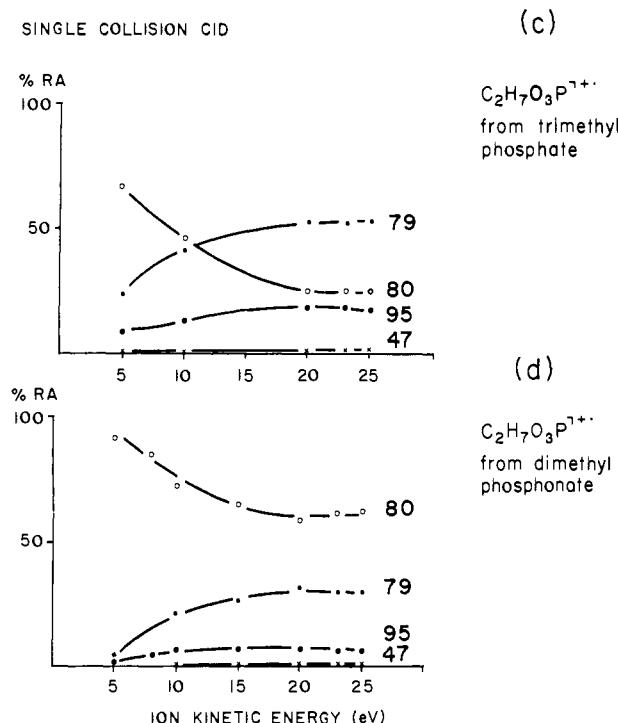


Figure 1. Fragmentation as a function of energy shown in the form of breakdown graphs for the $[M - CH_2O]^{+}$ ion of trimethyl phosphate (c) and the molecular ion of dimethyl phosphonate (d) recorded by energy-resolved mass spectrometry under single-collision conditions.

Loss of CH_2O from positively charged trimethyl phosphate produces an ion with hydrogen bound either to phosphorus or to one of the oxygen atoms. The two most probable tautomeric structures,¹⁸ as well as the fragmentation mechanisms leading to them, are shown in Scheme I. The phosphite structure (c) would be a result of a symmetry-allowed 1,4-hydrogen shift to the phosphoryl oxygen, whereas the phosphonate structure (d) requires a formal symmetry-forbidden 1,3-hydrogen shift to phosphorus or two consecutive symmetry-allowed 1,2-hydrogen shifts. In order to decide between these possibilities, the fragmentation characteristics of the $[M - CH_2O]^{+}$ ion of trimethyl phosphate were compared with those of a reference ion, which was obtained by ionizing dimethyl phosphonate. We assume that this ion at least has structure d.

High-energy daughter ion spectra of the molecular ion of dimethyl phosphonate (d) and the ion derived from the molecular ion of trimethyl phosphate via the loss of CH_2O are shown in Table I. The spectra are very similar, the only difference being the relative intensity of the peak at *m/z* 80, which arises by the loss

(18) A hydrogen shift to a methoxy oxygen would lead to a third structure. This ion is expected to be significantly less stable than either c or d owing to localization of the charge, and it is expected to lose CH_3OH readily. This was not observed. Therefore, this structure cannot make a significant contribution if it is involved at all.

of CH_2O . This reaction is the lowest energy process and is therefore usually excluded from consideration of the collisional activation data. This is because the lowest energy processes are often especially sensitive to the initial internal energy of the ion, that is, the energy of the ion *prior to excitation*.^{9,17} Therefore, the spectra shown in Table I could be interpreted to be due to the same ion with different internal energies.

Because collision-induced dissociation at a fixed energy gives an ambiguous result for the structural analysis in hand, more detailed insights were sought from energy-resolved mass spectrometry. This experiment yielded breakdown graphs which are shown in Figure 1. Similarities are seen in fragment ion abundances at low collision energy (and hence low internal energy), and this parallels the behavior observed in the MIKES spectra. However, when the full curves are considered, the behavior of the selected ions is clearly different. These differences in breakdown graphs could be due to different ion structures or to quite different initial internal energies.¹⁰ Four lines of evidence support the assignment of different structures to the ions producing the curves c and d. First, if the structures of the ions were the same, the initial internal energy of ion d would have to be very much smaller than that of ion c since formation of m/z 80 is the lowest energy process. This is not reasonable because the fragmentation threshold for the molecular ion of dimethyl phosphonate (d) is only 0.7 eV,¹⁹ and hence, the average initial internal energy of the ions which reach the collision region without fragmenting must be less than 0.7 eV. This is much less than the estimated change in energy deposition on varying the collision energy from 5 to 28 eV.²⁰ Second, the data just given require that if the structures of the ions producing the breakdown graphs (c and d) were the same, the curves of the fragment ions m/z 79 and 80, which cross each other in the low-energy part of graph c, should cross also in graph d, even if the initial internal energy of the ions were as different as possible (in the limits zero and the fragmentation threshold). They do not do so. Furthermore, not only do the relative intensities of the ions m/z 80 and 79 differ in these curves, but there are other differences as well. For example, the ratio of the relative intensities of the peaks at m/z 79 and 95 is larger for d at all collision energies above 10 eV, being about 5.5:1 for d but 3.0:1 for c at 25 eV. A third point in support of the conclusion that structural differences are responsible for the behavior seen in Figure 1 comes from comparing the breakdown graph of the $[\text{M} - \text{CH}_2\text{O}]^+$ ion of trimethyl phosphate measured at 40 °C ion source temperature with that of the molecular ion of dimethyl phosphonate (d) measured at 190 °C. Under these conditions, the breakdown graphs should resemble each other more closely, if the difference between them is due to different internal energies of the fragmenting ions, and not to different structures: as seen in Figure 2, ion c would have a higher internal energy than the ion d, and this difference is decreased by increasing the ion source temperature from 40 to 190 °C. However, temperature changes did not have any discernible effect on the breakdown graphs. A fourth and final argument for the fact that Figure 1 represents ions which differ in structure comes from the fragmentation of the molecular ion of trimethyl phosphate. This ion fragments exclusively via the ion $[\text{M} - \text{CH}_2\text{O}]^+$ in low-energy CID.²¹ The activation energy to form this ion is 0.8 eV.¹⁹ Therefore, the $[\text{M} - \text{CH}_2\text{O}]^+$ ion formed in CID will have some 0.8 eV less internal energy than the $[\text{M} - \text{CH}_2\text{O}]^+$ ion generated

(19) Activation energies were obtained by subtracting the appearance energies of the fragments of c from its appearance energy, and the appearance energies of the fragments of d from the ionization potential of dimethyl phosphonate. Appearance energies and ionization potentials were obtained from: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data*, 1977, 6, Suppl. 1.

(20) The exact distribution of energies deposited in low-energy collisions is not known, but the average energy deposited is known to vary from about 25 to 80% of the theoretical maximum (the center-of-mass kinetic energy; see ref 10 and 13). If we assume that the average internal energy deposited in the ion in this experiment is 25% of the theoretical maximum through the whole energy scale, the internal energy range represented in Figure 1 would be about 1.7 eV.

(21) Kenttämäa, H. I.; Cooks, R. G., to be submitted for publication.

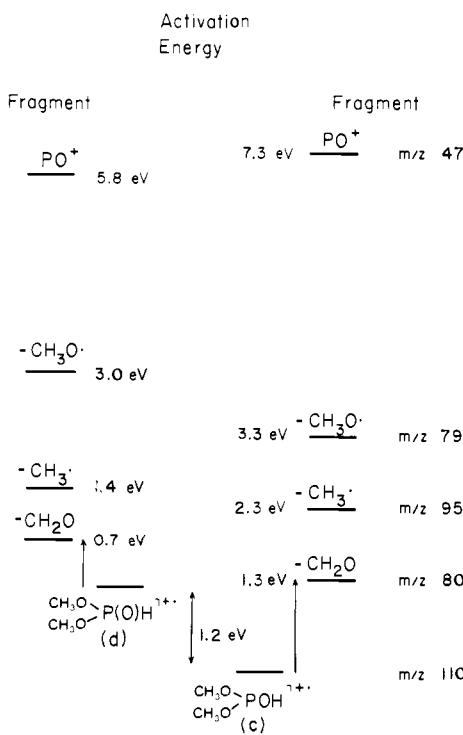


Figure 2. Activation energies for formation of the most abundant fragment ions from ionized dimethyl phosphite (c) and dimethyl phosphonate (d).

in the ion source and excited by collision.²² Thus, by measuring the breakdown graph for the molecular ion of trimethyl phosphate, one is also measuring that for the $[\text{M} - \text{CH}_2\text{O}]^+$ ion with less initial internal energy than the $[\text{M} - \text{CH}_2\text{O}]^+$ ion generated in the ion source. The breakdown graph obtained in this way was very similar to that obtained for the $[\text{M} - \text{CH}_2\text{O}]^+$ ion generated in the ion source, and only a slight shift was seen in the cross point of the curves for m/z 79 and 80 to a higher collision energy (from about 10 to 14 eV, which corresponds approximately²⁰ to 0.3 eV decrease in internal energy). Thus, no abnormal sensitivity of fragmentation behavior toward internal energy of the fragmenting ion could be observed.

On the basis of these results, we ascribe the different breakdown graphs to different ion structures or mixtures of isomers, and not to different initial internal energies of the ions sampled. It is also concluded that the structure of the $[\text{M} - \text{CH}_2\text{O}]^+$ ion of trimethyl phosphate is c, contrary to earlier assumptions.⁶ This ion arises via a symmetry-allowed 1,4-hydrogen shift to phosphoryl oxygen. The tendency to form P-OH groups has earlier been observed to be extremely strong for ionized phosphate esters,^{11,23} apparently because it allows a more complete delocalization of the charge.⁷ This behavior is also seen in the fragmentation of ions c and d: the loss of CH_2O is much more favorable for d which has a phosphoryl oxygen available for hydrogen transfer, whereas ion c, which already contains a protonated phosphoryl oxygen, preferentially loses CH_3O^- in a simple bond cleavage even at modest collision energies.

The enhanced abundance of m/z 95 (due to loss of $\text{CH}_3\cdot$) from the $[\text{M} - \text{CH}_2\text{O}]^+$ ion of trimethyl phosphate is also consistent with the proposed structure c. Specifically, the loss of a methyl radical from this ion requires an activation energy of about 2.3 eV,¹⁹ whereas the corresponding reaction for d requires only about 1.4 eV internal energy,¹⁹ but occurs in much lower abundance. The loss of $\text{CH}_3\cdot$ can occur via a fast direct bond cleavage for c,

(22) Possible differences in internal energy distributions of the molecular ion and the $[\text{M} - \text{CH}_2\text{O}]^+$ ion (fragmentation thresholds 0.9 and 1.3 eV, respectively) generated in the ion source tend further to increase this difference.

(23) (a) Desmarchelier, J. M.; Wustner, D. A.; Fukuto, T. R. *Residue Rev.* 1976, 63, 77. (b) Kenttämäa, H. I., ref 11, p 575.

whereas, in the case of d, a rearrangement must be invoked to avoid the formation of an oxenium cation. A higher activation energy but higher reaction rate at high internal energies of the fragmenting ion, as observed for the $\text{CH}_3\cdot$ loss from the $[\text{M} - \text{CH}_2\text{O}]^+$ ion, is consistent with a direct bond cleavage, and thus with the proposed structure c (see also Scheme II below).

The difference in stability of the tautomeric ions c and d can be estimated. A correlation obtained between the proton affinity and ionization potential of trivalent phosphorus esters²⁴ allows one to calculate the approximate proton affinity of a trivalent phosphorus ester if the ionization potential is known, and vice versa:

$$\text{PA} = 0.853(1920 - \text{IP}) \quad (\text{kJ mol})$$

The proton affinity of dimethyl phosphite has been determined to be 893 kJ/mol.² Thus, the ionization potential of dimethyl phosphite is about 9 eV. The ionization potential of dimethyl phosphonate is significantly higher, 10.5 eV.¹⁹ The stability difference in the neutrals corresponding to the ions c and d is 27 kJ/mol (0.28 eV) in favor of d, as mentioned above.² Therefore, the difference in stabilities of ionized c and d is estimated to be 1.2 eV (116 kJ/mol) in favor of c. This difference is mainly determined by the large difference in ionization potentials of dimethyl phosphonate and dimethyl phosphite. Thus, although dimethyl phosphite is the less stable neutral tautomer, the ionized form is significantly more stable than the phosphonate tautomer.

An approximate energy diagram for the tautomeric ions c and d is shown in Figure 2.^{19,25} The fragmentation threshold for ion c (1.3 eV) is almost equal to the difference in the heats of formation of c and d (1.2 eV). Based on this, ions d, which have enough energy to isomerize to c, should also have enough energy to fragment from this structure, even if the activation energy for isomerization were very small. Isomerization of d to c, followed by fragmentation, would be expected to compete with direct fragmentation from structure d especially in ions excited by low-energy collisions, where the internal energy of the ions is too low for direct bond cleavages to be competitive with isomerization. At higher collision energies, a direct bond cleavage, loss of $\text{CH}_3\text{O}\cdot$, becomes competitive, and the relative amount of isomerization decreases owing to its unfavorable frequency factor. Therefore, the tautomers are best differentiated by using high collision energies, where the relative amount of isomerization is minimized. This is a particularly clear case of a widely accepted generalization.¹⁰

A comparison of the MIKES spectra of c and d (Table I) with their breakdown graphs (Figure 1) reveals that, contrary to general expectation, a comparable amount of energy is deposited in these two ions in both low- and high-energy collisions. A similar observation has recently been made for the molecular ion of triethyl phosphate¹⁶ and for $\text{C}_3\text{H}_6\text{O}^+$ ions.¹²

The loss of $\text{CH}_3\cdot$ from d probably occurs via a rearrangement reaction, as mentioned above. The activation energy for the loss of $\text{CH}_3\cdot$ from d added to the stability difference between the tautomers c and d (which would appear as extra internal energy of d if it isomerized to c prior to the loss of $\text{CH}_3\cdot$) is equal, within experimental error, to the activation energy for the loss of $\text{CH}_3\cdot$ from c (2.6 and 2.3 eV, respectively). Thus, we propose that the rearrangement reaction involved when $\text{CH}_3\cdot$ is lost from d is the isomerization $d \rightarrow c$ (Scheme II). If this is so, then the activation energy for this reaction (1.4 eV) represents the upper limit for the activation energy of tautomerization $d \rightarrow c$. The fact that the loss of CH_2O occurs spontaneously after isomerization of d to c (see above) confirms that the isomerization barrier must be at or above the fragmentation threshold of d, because this corresponds to the activation energy for CH_2O loss. Thus, the activation energy for isomerization $d \rightarrow c$ is estimated to be between 0.7 and 1.4 eV, the lower limit coming from the threshold for fragmentation of d and the upper from the energy for $\text{CH}_3\cdot$ loss

Scheme II

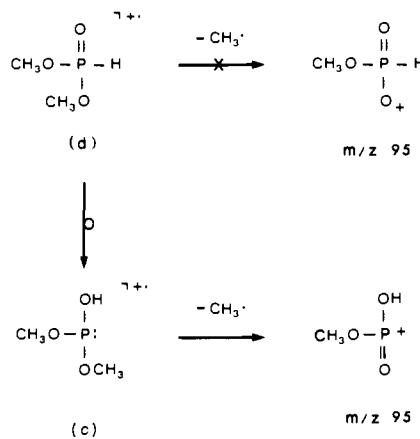


Table II. Breakdown Graphs for the Products of CH_2O Loss (m/z 80) from Ionized Dimethyl Phosphite (c) and Dimethyl Phosphonate (d) Recorded by Energy-Resolved Mass Spectrometry under Single-Collision Conditions

collision energy (eV)	fragment (m/z)	rel abundance (%) ^a	
		c	d
5	65	92	97
	47	6	3
	63	2	0.5
	65	91	95
	47	9	3
	63	0.4	2
10	65	85	91
	47	12	9
	63	3	0.3
	65	72	81
	47	24	15
	63	4	4
15	65	55	69
	47	33	20
	63	12	10
20	65	72	81
	47	24	15
	63	4	4
	65	55	69
	47	33	20
	63	12	10
26	65	72	81
	47	24	15
	63	4	4
	65	55	69
	47	33	20
	63	12	10

^a Percentage of the sum of the intensities of the three fragments.

from d. The loss of CH_2O from d could occur via two different routes: from d directly by a 1,4-hydrogen shift, and via preceding isomerization to c. If the latter one is the lowest energy process, then the isomerization barrier is equal to the activation energy for this reaction (0.7 eV). Some support for the possibility that the loss of CH_2O from d occurs via the $d \rightarrow c$ isomerization route is obtained by comparing the breakdown graphs of the products of CH_2O loss (m/z 80) from c and d. The two ions behave very similarly, each giving fragments m/z 65, 47, and 63. Furthermore, the relative intensities of these fragments vary with collision energy in a similar fashion (Table II). Referring to Figure 2, we summarize our conclusions from the single collision experiments by noting that the less stable phosphonate structure fragments almost exclusively via isomerization to the stable phosphite structure when gently activated (CH_2O loss and $\text{CH}_3\cdot$ loss); otherwise it fragments directly from structure d.

The breakdown graph of d changes dramatically when the average number of collisions each ion undergoes increases. At about 2 mtorr target pressure, where each ion d undergoes, instead of a single collision, an average of eight collisions,²⁶ the breakdown graph obtained for d is almost identical with that of c (Figure 3), and is also very similar to that recorded for c under single collision conditions (Figure 1). This suggests that when activated in this way d fragments almost exclusively via structure c. A sequence of small energy inputs will tend to favor isomerization reactions if these are energetically accessible. This point has been made previously for collision-induced dissociation.^{10,27} An ad-

(24) Hedges, R. V.; Houle, F. A.; Beauchamp, J. L.; Montag, R. A.; Verkade, J. G. *J. Am. Chem. Soc.* **1980**, *102*, 932.

(25) The assignment of the elemental compositions of the fragments of dimethyl phosphonate in ref 19 is incorrect; see Pritchard, J. G. *Org. Mass Spectrom.* **1970**, *3*, 163.

(26) The number of collisions is calculated from the path lengths and from an estimated collision cross section of 16 \AA^2 .

MULTIPLE COLLISION CID

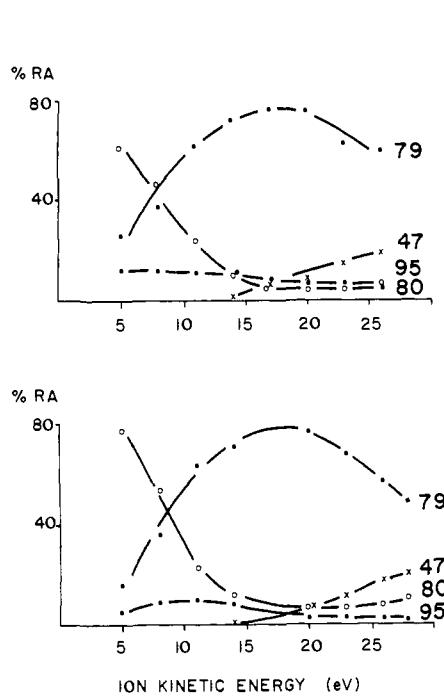
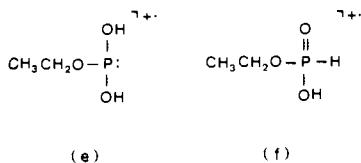


Figure 3. The breakdown graph of the $[M - \text{CH}_2\text{O}]^+$ ion of trimethyl phosphate (c) and the molecular ion of dimethyl phosphonate (d) recorded by energy-resolved mass spectrometry under multiple-collision conditions (2 mtorr of Ar).

ditional reason for similarity of the breakdown graphs is further decomposition of fragment ions, most notably fragmentation of the ion m/z 80 (the isomerization $d \rightarrow c$ is probably in most cases followed by fragmentation $c \rightarrow m/z$ 80; see above). However, this cannot be the only reason because of the following facts: (1) The change in the breakdown graph of d is dramatic when the number of collisions is increased, but that in the breakdown graph of c is very small. (2) The breakdown graph obtained for d in multiple-collision conditions is very similar to that obtained for c in single- as well as in multiple-collision conditions. (3) The difference in the relative abundances of the ions of m/z 80 and 79 in the single-collision CID spectra do not show up in relative abundances of their daughters in the multiple-collision CID spectra. For example, d should show a smaller ratio for the relative intensities of the ions of m/z 79 to 47 (a major fragmentation product of m/z 80 at higher energies), which is not the case (the ratio is 0.30 for d and 0.32 for c at 26-eV collision energy).

Another ion which is an isomer of the tautomers c and d was obtained from triethyl phosphate upon electron impact ionization followed by consecutive losses of CH_3CHO and C_2H_4 . The two most probable tautomeric structures in this case are e and f



generated by reactions analogous to those given in Scheme I. The fragmentation of this ion is considerably different from that of (c) and (d) (m/z 92(5%), m/z 83(39%), m/z 82(100%), m/z 81(8%), m/z 65(6%), m/z 29(22%), m/z 28(5%)). The predominant losses are assigned as $\text{C}_2\text{H}_3\cdot$ and C_2H_4 (to produce the ion m/z 82), which clearly show the presence of an ethyl group. The loss of H_2O (to produce the ion m/z 92) indicates that at least two hydroxyl groups are attached to phosphorus.^{5,28} Fur-

Scheme III

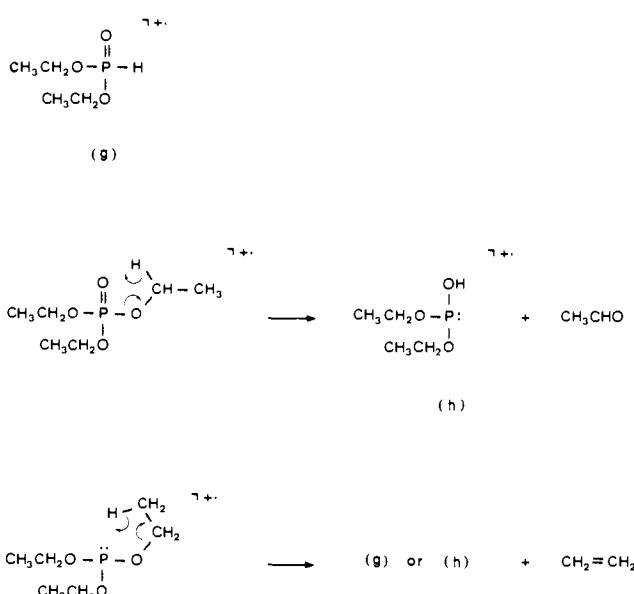


Table III. Low-Energy CID Spectra for the $[M - \text{C}_2\text{H}_4]^+$ Ion of Triethyl Phosphate (h), the $[M - \text{C}_2\text{H}_4]^+$ Ion of Triethyl Phosphite (g or h), and the Molecular Ion of Diethyl Phosphonate (g)^a

<i>m/z</i> (%)		
h	g or h	g
111 (100)	111 (91)	111 (100)
110 (34)	110 (26)	110 (25)
109 (5)	109 (3)	109 (4)
94 (11)	94 (12)	94 (15)
92 (7)	92 (4)	92 (7)
83 (39)	83 (35)	83 (42)
82 (98)	82 (100)	82 (83)
81 (7)	81 (5)	81 (4)
66 (14)	66 (13)	66 (16)
45 (6)	45 (6)	45 (8)
29 (19)	29 (16)	29 (16)

^aSingle-collision conditions and ca. 20 eV collision energy.

thermore, the loss of C_2H_4 is greatly favored over the loss of $\text{C}_2\text{H}_3\cdot$ although the latter reaction leads to an even-electron ion, and is by far the most favored fragmentation reaction of the molecular ions of most trialkyl phosphates,^{7,29} as well as, for example, of diethyl phosphonate.³⁰ (Fragmentations involving hydrogen migration are enhanced by the presence of a phosphoryl oxygen in the case of tautomers c and d, as shown above.) For all these reasons, we conclude that the most probable structure for the fragmenting ion in question is e rather than f, in contrast to earlier assumptions for similar ions.^{1,5}

Turning to the ethyl homologues of the phosphonate and phosphite ions, one finds that the results obtained for diethyl phosphonate radical cation and its tautomer differ dramatically from those obtained for the dimethyl analogues c and d. Tautomeric diethyl phosphonate ions were obtained from three different sources. Diethyl phosphonate ion (g) (Scheme III) was prepared by direct ionization of the corresponding neutral. The loss of acetaldehyde from triethyl phosphate produces an ion with the same or a tautomeric structure. Based on the results obtained for the dimethyl esters above, the phosphite tautomer (h) is the most probable initial product (Scheme III) (this reaction corresponds to the loss of CH_2O from trimethyl phosphate). Finally, the loss of C_2H_4 from triethyl phosphate, on the other hand, could produce either one of the tautomers, g or h, or a mixture of them (Scheme III). These three ions (the molecular ion of diethyl

(27) (a) "Collision Spectroscopy"; Cooks, R. G., Ed.; Plenum Press: New York, 1978; p 379. (b) Blom, K.; Munson, B. *J. Am. Chem. Soc.* 1983, 105, 3793.

(28) Sass, S.; Fischer, T. L. *Org. Mass Spectrom.* 1979, 14, 257.

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

(30) Pritchard, J. G. *Org. Mass Spectrom.* 1970, 3, 163.

phosphonate, the $[M - C_2H_4O]^+$ ion of triethyl phosphate and the $[M - C_2H_4]^+$ ion of triethyl phosphite) all produce nearly identical breakdown graphs even under single-collision conditions (Table III). The lowest known activation energy for the fragmentation of the $[M - C_2H_4O]^+$ ion of triethyl phosphate is 1.9 eV,¹⁹ corresponding to the loss of C_2H_4 , and this is probably the lowest energy process for this ion (the activation energy for the other favored reaction, loss of C_2H_3 , is 2.0 eV).¹⁹ This activation energy is much higher than the fragmentation threshold of dimethyl phosphonate ion (d) and its tautomer (c) (0.7 and 1.3 eV, respectively), which makes it more probable in the former case that the isomerization barrier is below the fragmentation thresholds of the tautomers. Indeed, the results obtained for the ethyl homologues indicate that isomerization to a common structure or mixture of structures occurs *prior to* decomposition.³¹ This is contrary to the behavior of the methyl homologues, which retain their structural identity under the same experimental conditions.

Conclusion

Ionized dimethyl phosphite is significantly more stable than the phosphonate tautomer, in striking contrast to the relative

(31) The breakdown graph obtained for the molecular ion of diethyl phosphonate shows a slightly more intense peak at m/z 111 than do the ions with the same composition obtained from different sources. The formation of m/z 111 (loss of C_2H_3) requires two hydrogen shifts. It fragments further to m/z 83. The formation of all the other abundant ions (m/z 110, 82; see Table II) requires a single hydrogen shift. Furthermore, the corresponding peaks are only minor or totally absent in the electron impact ionization mass spectrum of diethyl phosphonate (see ref 30), although the energy resolved mass spectrometry experiment showed them to arise from high-energy processes (which usually produce more abundant peaks to electron impact ionization mass spectra than low-energy CID spectra), thus indicating that they, in fact, are the result of a preceding slow isomerization $g \rightarrow h$. In the ion source, because of competition between fast direct bond cleavages and rearrangement reactions, isomerization does not occur to a significant extent. Thus, it can be concluded that also here, as in the case of c and d, fragmentation via hydrogen transfers is preferred for the phosphonate structure.

stabilities of the corresponding neutral molecules. This stability difference, as well as the preferred formation of the more stable of these tautomers in the fragmentation of ionized trimethyl phosphate, supports and rationalizes the earlier evidence^{11,23} of a very strong tendency of organophosphorus ester ions for formation of the P-OH group. One of the forces driving gas-phase reactions of ionized phosphorus esters seems to be generation of the P-OH structure, whereas P=O bond formation plays a corresponding role in reactions of neutral phosphorus esters. In contrast to the behavior of the methyl tautomers, ionized diethyl phosphonate and phosphite tautomers are not distinguishable, and available thermochemical data explain this.

This work clearly demonstrates the capability of energy-resolved mass spectrometry in differentiating tautomeric ion structures. In addition, the results show the importance of using low target pressures in collision-induced dissociation when closely similar ion structures are compared. Because of enhanced isomerization under multiple-collision conditions, structural identity of ionized dimethyl phosphonate and dimethyl phosphite is lost.

Even in such simple systems as studied here, the ion chemistry is surprisingly rich. Additional mass spectrometric techniques now emerging, such as the ability to carry out sequential collision-induced dissociations by utilizing collision chambers situated in different parts of a tandem mass spectrometer,³² will be useful in further research on the phenomena revealed here.

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(32) Burinsky, D. I.; Cooks, R. G.; Chess, E. K.; Gross, M. L. *Anal. Chem.* 1982, 54, 295.

Electron Spin Resonance Study of Tris[2-aminobenzenethiolato(2-)-S,N]technetium(VI) and -rhenium(VI) Chelates: Evidence for Molecular Aggregation in Solution

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Abstract: ESR measurements at ca. 9.15 GHz and in the range 2–4 GHz have enabled the effects of concentration and solvent composition on the spectra of frozen solutions of trigonal-prismatic tris[2-aminobenzenethiolato(2-)-S,N]technetium(VI) and -rhenium(VI) complexes to be interpreted in terms of the breakdown of molecular aggregates. In the case of $Tc(abt)_3$, this dissociation gives the monomeric species, while $Re(abt)_3$ appears to give a mixture of trimeric and monomeric species. The spectra arising from the monomeric species are best interpreted by almost isotropic g and A values but with a subtle interplay of anisotropic line width effects. The extent of the delocalization of the unpaired electron in the $2a_2'$ molecular orbital onto the ligands is indicated by the effects on the ESR spectra of intermolecular exchange interactions between $Re(abt)_3$ molecules, where the Re ions are probably ca. 10 Å apart. This is a rare example of intermolecular exchange interactions without a direct-bonded pathway.

The use of technetium compounds as radiopharmaceuticals has stimulated interest in the physical and chemical properties of technetium complexes in general. In addition, the location of technetium in the periodic table between molybdenum and ru-

thenium along the 4d transition series and with the same d electron configuration as manganese (3d) and rhenium (5d) enables comparisons to be made between the behavior of technetium and these other chemically very interesting metallic elements.

An X-ray diffraction study of the complex tris[2-aminobenzenethiolato(2-)-S,N]technetium(VI), $Tc(abt)_3$ (I), showed that the technetium ion was six-coordinate in a trigonal-prismatic

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