J. Am. Chem. Soc. **1992**, *114*, 2027-2031

Table IV. Gas-Phase Heats of Formation (kJ mol^{-1}; Rounded Off to the Nearest 5 kJ mol^{-1}) of Reactants, Intermediates, and Products Discussed in the Text (Except As Discussed in the Appendix, Values Are Taken from Reference 13)

$CH_3OCH_2CH_2OH^{\bullet+}$ ($\mathbf{1}^{\bullet+}$)	560
$^{\bullet}CH_2OCH_2CH_2OH_2^{+}$ (**6**)	550
$^{\bullet}CH_2O^{+}(CH_3)CH_2OH$ (**8**)	520
$(CH_3)_2O^{+}CH_2O^{\bullet}$ (**9**)	495
oxetane radical cation + H_2O	615
$CH_3OCH_3^{\bullet+}$ + $CH_2{=}O$	675
oxirane + $^{\bullet}CH_2OH_2^{+}$	775
$(CH_3)_2OH^{+}$ + $^{\bullet}CH{=}O$	590
$CH_3OCH_2^{+}$ + $^{\bullet}CH_2OH$	620
propionaldehyde$^{\bullet+}$ + H_2O	530
methyl vinyl ether radical cation + H_2O	520
$CH_3CH_2CO^{+}$ + $H^{\bullet}$ + H_2O	570
protonated acrolein + $H^{\bullet}$ + H_2O	620
protonated oxirane + $^{\bullet}CH_2OH$	660

same as that of dimethyl ether. This gives a value slightly lower than that of $\mathbf{1}^{\bullet+}$, $\Delta H_f(\mathbf{6}) = 550$ kJ mol^{-1}. Heats of formation of relevant reactants, products, and intermediates are summarized in Table IV.

Acknowledgment. We are grateful to Steen Hammerum for the gift of $(CD_2O)_n$ and for much useful dialogue. This work was supported by the CNRS, NSF Grant CHE 88-2086, and a Fulbright Travel Grant to T.H.M.

Registry No. 1a, 109-86-4; **1b**, 138408-76-1; **1c**, 86012-98-8; **1d**, 51255-53-9; **1e**, 138408-77-2; **1f**, 97840-77-2; **1g**, 86012-99-9; **1h**, 51255-54-0; **1i**, 138408-78-3; **1j**, 138408-79-4; **1k**, 138408-80-7; **2b**, 138408-89-6; **2c**, 138408-90-9; **5a**, 4484-61-1; **5b**, 138408-84-1; **5c**, 138408-85-2; **5d**, 138408-86-3; **6a**, 86023-99-6; **6b**, 138408-81-8; **6c**, 138408-82-9; **6d**, 138408-83-0; **7a**, 17009-82-4; **7b**, 138408-91-0; **7c**, 138408-92-1; **7d**, 138408-93-2; **7e**, 138408-94-3; **7f**, 138408-95-4; **7g**, 138408-96-5; **7h**, 138408-97-6; **7i**, 138408-98-7; **7j**, 138408-99-8; **7k**, 131295-07-3; **7l**, 138409-00-4; **7m**, 138409-01-5; **7n**, 138409-02-6; **7o**, 138409-03-7; **7p**, 138409-04-8; **7q**, 138409-05-9; **7r**, 138409-06-0; **7s**, 138409-07-1; **8**, 138408-87-4; **10**, 138408-88-5; methyl (methoxymethoxy)acetate, 50918-08-6; methoxyacetaldehyde, 10312-83-1; methyl glycolate, 96-35-5; oxetane radical cation, 74181-62-7; ethylene glycol, 107-21-1.

Supplementary Material Available: Tabulated CAD spectral data for $C_3H_6O^{\bullet+}$ isomers, isotopic analogues of methanol conjugate acids, and M − formyl ions from **2a–c** (1 page). Ordering information is given on any current masthead page.

A Remarkably Stable Organic Radical Cation: The Distonic Isomer of the Unstable Radical Cation of Dimethyl Propyl Phosphate

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Received July 9, 1991

Abstract: A new isomer of the radical cation of dimethyl propyl phosphate has been synthesized in the gas phase by transferring ionized ethylene to trimethyl phosphate. Examination of the dissociation reactions of this ion suggests that it is covalently bound, and has spatially separated radical and charge sites (a distonic ion). In contrast to most known radical cations with a formally localized charge (when using classical valence electron description), this ion is remarkably unreactive toward strong bases, nucleophiles, and reductants. A slow transfer of ionized ethylene is observed for phosphorus nucleophiles only. This reaction is proposed to take place by a radical-type mechanism. These findings contrast sharply with the recent suggestion that distonic ions are expected to be highly reactive toward neutral molecules in the gas phase.

Introduction

Gaseous radical cations with spatially separated radical and charge sites, the so-called distonic ions, have attracted considerable interest during the last nine years.[1] Many distonic ions are thermodynamically as well as kinetically more stable than their conventional counterparts, molecular ions generated by removal of an electron from a stable neutral molecule.[1] However, the current knowledge on the properties of gaseous distonic ions with the charge and radical sites separated by at least one heavy atom is almost exclusively limited to unimolecular reactions. Thus far, bimolecular reactions of four β-distonic ions and one γ-distonic ion (two heavy atoms between the charge and the radical site, when written using the valence electron formalism) have been investigated.[1-5] These ions include two protonated radicals ($^{\bullet}CH_2CH_2NH_3^{+}$ and $^{\bullet}CH_2CH_2O^{+}(H)CH_3$),[1,2] and the ring-opened forms of ionized cyclopropane[3] ($^{\bullet}CH_2CH_2CH_2^{+}$), ionized trimethylene oxide[4] ($^{\bullet}CH_2CH_2O^{+}{=}CH_2$), and ionized cyclobutanone ($^{\bullet}CH_2CH_2CH_2C{=}O^{+}$).[5] The results obtained[1-5] suggest that bimolecular reactions predominantly involve the charge site of these ions. Deprotonation dominates the chemistry of the acidic ions (protonated radicals).[1-4] For the ion $^{\bullet}CH_2CH_2O{=}CH_2^{+}$, addition of the attacking nucleophile to the unsaturated charged center has been proposed to be the initial step in the reactions with acetonitrile and pyridine.[4b]

This study focuses on the synthesis and properties of a novel gaseous distonic ion that does not have acidic functional groups or unsaturation near the charge site. This ion was found to be nearly unreactive toward strong bases, nucleophiles, and reductants, in sharp contrast with the recent suggestion[4b] that distonic ions may be highly reactive in ionic as well as in radical reactions.

Experimental Section

The prototype Extrel FTMS 2001 mass spectrometer used in this study has a differentially pumped 2-in. dual cell aligned collinearly with a magnetic field produced by a 2.8-T superconducting magnet. The dual cell is pumped with two turbomolecular pumps (Balzars TPU 330). The base pressure in both sides of the cell is less than 1×10^{-9} Torr, as measured by an ionization gauge on each side. The trapping plates parallel to the magnetic field were kept at +2 V, including the conductance limit plate separating the two cells. The conductance limit plate was grounded for 100–200 μs when ions were transferred from one side of the dual cell into the other side. Reagents were added to the system

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(1) Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123.

(2) Busch, K. L.; Nixon, W. B.; Bursey, M. M. *J. Am. Chem. Soc.* **1978**, *100*, 1621.

(3) (a) Gross, M. L.; McLafferty, F. W. *J. Am. Chem. Soc.* **1971**, *93*, 1267. (b) Lias, S. G.; Buckley, T. J. *Int. J. Mass Spectrom. Ion Processes* **1984**, *56*, 123. (c) Sack, T. M.; Cerny, R. L.; Gross, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 4562. (d) Rusli, R. D.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 535.

(4) (a) Baumann, B. C.; McLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 7927. (b) Wittneben, D.; Grutzmacher, H.-F. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 545.

(5) Stirk, K.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1991**, *113*, 5880.

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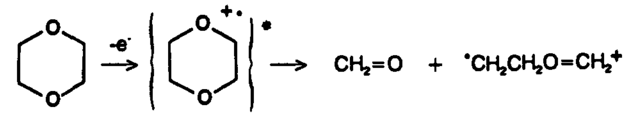
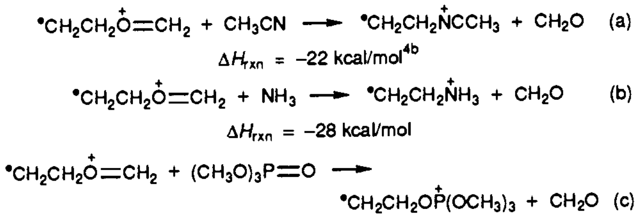
Scheme I



Scheme II



$$\cdot CH_2CH_2\overset{+}{O}{=}CH_2 + CH_3CN \longrightarrow \cdot CH_2CH_2\overset{+}{N}CCH_3 + CH_2O \quad (a)$$
$$\Delta H_{rxn} = -22\ \text{kcal/mol}^{4b}$$
$$\cdot CH_2CH_2\overset{+}{O}{=}CH_2 + NH_3 \longrightarrow \cdot CH_2CH_2\overset{+}{N}H_3 + CH_2O \quad (b)$$
$$\Delta H_{rxn} = -28\ \text{kcal/mol}$$
$$\cdot CH_2CH_2\overset{+}{O}{=}CH_2 + (CH_3O)_3P{=}O \longrightarrow \cdot CH_2CH_2O\overset{+}{P}(OCH_3)_3 + CH_2O \quad (c)$$

by using a Varian leak valve, a set of pulsed valves, or a prototype heated batch inlet system equipped with a leak valve. Nominal reagent gas pressures were (0.4–3) × 10^{-7} Torr.

Primary ions were generated by 15–70-eV electron ionization, and collisionally cooled prior to studying their reactions. Collisionally activated dissociation with argon collision gas (nominal pressure 1 × 10^{-7} Torr) was carried out for isolated ions by using an excitation pulse with a fixed amplitude (0.08 V_{p-p}) and a variable duration (≤1 ms). The subsequent reaction time was 100 ms. During this time period, the kinetically excited ions undergo activating collisions with argon and consequently decompose. The laboratory kinetic energy of the ions after acceleration has been estimated by others[6] to be about 0.5 that computed according to the infinite parallel plate approximation, $E_{ion} = q^2V^2t^2/8md^2$, where q is the ionic charge, V is the amplitude of the rf excitation pulse (0.08 V), t is the rf pulse duration, m is the ionic mass, and d is the distance between the excitation plates (4.7 cm). The average number of activating collisions is two to four for an ion of m/z 168 with a kinetic energy in the range 5–25 eV (laboratory frame), as estimated using the kinetic theory of gases.

For reaction rate calculations, the pressure readings obtained on the ionization gauges on each side of the dual cell were adjusted according to correction factors obtained from examination of several well-characterized reactions with known[7] rate constants (e.g., $CH_3CH_2OH_2^+$ + CH_3CH_2OH[7a] and $P(OH)_4^+$ + $(CH_3CH_2O)_3P{=}O$[7b]). The precision of the rate measurements is better than ±5%; the accuracy is estimated to be better than ±50%. All the spectra shown are an average of more than 15 spectra acquired using an excitation sweep with an amplitude of 105 V (V_{p-p}), a bandwidth of 2.7 MHz, and a sweep rate of 3.2 kHz/μs. The digitizer rate was 5.3 MHz. The spectra were recorded as 32k data points subjected to one zero fill before Fourier transformation.

Results and Discussion

Transfer of Ionized Ethylene from $\cdot CH_2CH_2O^+{=}CH_2$ to Nucleophiles. Gas-phase reactions of the distonic ion $\cdot CH_2CH_2O^+{=}CH_2$ (m/z 58) were investigated with different neutral reagents since this ion is a potentially useful tool for the synthesis of gaseous β-distonic ions. The ion $\cdot CH_2CH_2O^+{=}CH_2$ can be generated[4] by dissociation of ionized 1,4-dioxane (Scheme I). It is known[4] to transfer ionized ethylene to acetonitrile, accompanied by the loss of formaldehyde (Scheme II, reaction a). The product ion was recently verified[4b] to have the structure $CH_3CN^+CH_2CH_2^\cdot$. With pyridine, however, no transfer of ionized ethylene was observed.[4b]

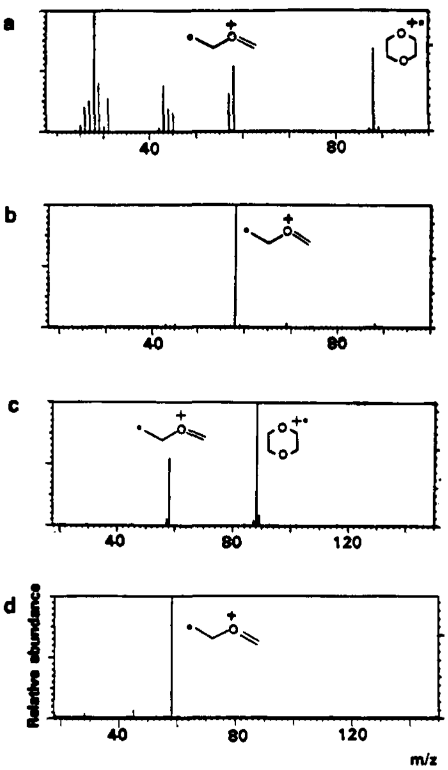


Figure 1. (a) 50-eV electron ionization mass spectrum of 1,4-dioxane in the source cell. (b) Isolation of the ion of m/z 58 in the source cell. (c) Reaction of the ion of m/z 58 with 1,4-dioxane (nominal pressure 1 × 10^{-7} Torr) for 1 s in the source cell. (d) Storage of the ion of m/z 58 in the analyzer cell (nominal pressure 1 × 10^{-9} Torr) for 1 s after generation and isolation in the source cell as shown in (a) and (b).

Table I. Thermochemical and Physical Values Used in This Work

compound	ΔH_f	PA[a] (kcal/mol)	IE[a] (eV)
NH_3	−11[a]	204	10
$s\text{-}C_4H_9NH_2$	−25[a]	221	~9
$(CH_3CH_2)_3N$	−22[a]	232	7.5
$(CH_3O)_3P$	−167[a]	221	~8.5
$(CH_3CH_2O)_3P$	−193[a]	~226[b]	~8.4
CH_3SSCH_3	−5.8[a]	196	~7.4
$(CH_3O)_3P{=}O$	−265[a]	212	10.0
$CH_2{=}CH_2$	12.5[a]		
$CH_2{=}CH^\cdot$	63[a]		
CH_2O	−26[a]		
CH_3CN	18[a]		
$\cdot CH_2CH_2O^+{=}CH_2$	198[c]		
$(CH_3O)_3PH^+$	−22[a]		
$s\text{-}C_4H_9NH_3^+$	120[a]		
$(CH_3CH_2)_3NH^+$	111[a]		
$CH_3SSCH_3^{\cdot +}$	165[a]		
$\cdot CH_2CH_2NH_3^+$	185[d]		
$CH_3CN^+CH_2CH_2^\cdot$	(220)[e]		
$(CH_3O)_3P^+OCH_2CH_2^\cdot$	(−70)[f]		

[a] Reference 10. [b] Reference 11. [c] Reference 12. [d] Reference 13. [e] Reference 4b. [f] Estimated using AM1.

The distonic ion $\cdot CH_2CH_2O^+{=}CH_2$ was generated by electron ionization induced dissociation of 1,4-dioxane in one side of the differentially pumped dual cell of a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR). Investigation of the reactions of this ion is best carried out without the presence of the neutral precursor since the ion reacts with 1,4-dioxane (Figure 1). Therefore, the ion was transferred into the other side of the dual cell for examination of its reactions with the neutral reagents of interest. The distonic ion was isolated by ejecting all the unwanted ions from the cell through the use of several single frequency pulses and frequency sweeps, collisionally cooled, and allowed to react for variable time periods with the neutral reagent present in the cell.

The ion $\cdot CH_2CH_2O^+{=}CH_2$ was observed to react at near collision rate (k_{ADO} = (1–4) × 10^{-9} cm^3 molecule^{-1} s^{-1})[8] with all

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(6) Grosshans, P. B.; Marshall, A. G. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 347.

(7) (a) Ikezoe, Y.; Matsuoka, S.; Takebe, M.; Viggiano, A. *Gas-Phase Ion Molecule Reaction Rate Constants Through 1986*; Maruzen Co., Ltd.: Tokyo, 1987. (b) Hodges, R. V.; McDonnell, T. J.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1327.

(8) (a) Chesnavich, W. J.; Su, T.; Bowers, M. T. *J. Chem. Phys.* **1980**, *72*, 2641. (b) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183. The polarizabilities were calculated according to the following reference: (c) Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149. The dipole moments were obtained from ref 9.

(9) *Tables of Experimental Dipole Moments*; McClellan, A. L., Ed.; Freeman and Co.: San Francisco, 1989; Vol. 3.

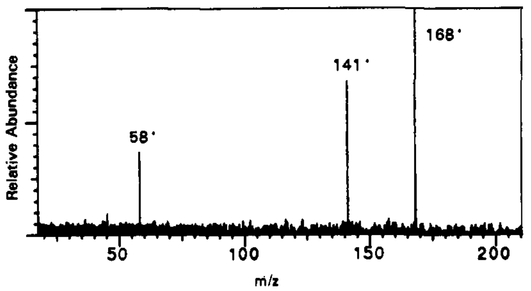
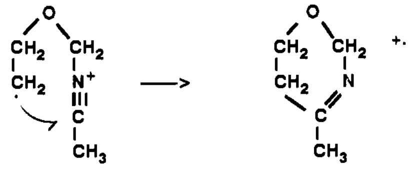


Figure 2. Products obtained when $^{\bullet}CH_2CH_2O^+{=}CH_2$ is allowed to react for 650 ms with trimethyl phosphate (nominal pressure 1.2×10^{-7} Torr).

of the neutral reagents studied, including SH_2, CD_2O, CH_3COOH, and $(CH_3O)_3P{=}O$ (Table I shows relevant thermochemical data for the neutral and ionic reagents). Two reaction channels are observed: transfer of ionized ethylene (Scheme II) and proton transfer (Figure 2). Especially noteworthy is the observation that $^{\bullet}CH_2CH_2O^+{=}CH_2$ transfers ionized ethylene to NH_3 (Scheme II, reaction b). This particular reaction cannot occur through the mechanism proposed[4b] earlier for transfer of ionized ethylene from $^{\bullet}CH_2CH_2O^+{=}CH_2$ to acetonitrile. It was suggested[4b] that acetonitrile initially attacks the positively charged methylene carbon, followed by formation of a cyclic intermediate through radical addition of the terminal ethylene carbon to the acetonitrile carbon (see structure b below). This mechanism is not feasible for ammonia since it would involve formation of hypervalent nitrogen. Transfer of ionized ethylene to ammonia is likely either to occur by an S_N2 mechanism at one of the ethylene carbons of $^{\bullet}CH_2CH_2O^+{=}CH_2$, or to involve transfer of ammonia to the radical site after formation of the initial addition product analogous to that shown below for acetonitrile (structure a).



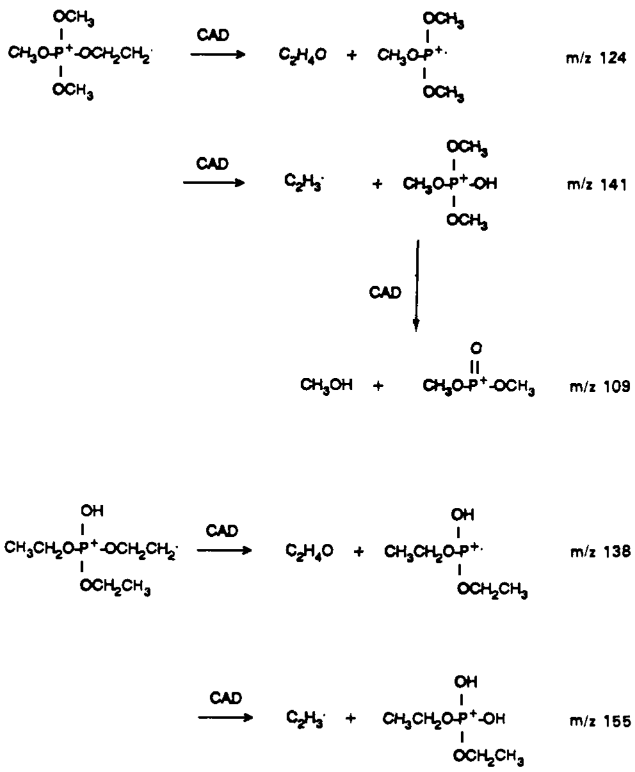
a b

Structure of the Product from Transfer of Ionized Ethylene to Trimethyl Phosphate. Reaction of $^{\bullet}CH_2CH_2O^+{=}CH_2$ with trimethyl phosphate occurs at about every second collision ($k_{obs} = 1.7 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}; collision rate or $k_{ADO} = 2.6 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}).[8] Two primary products are generated: protonated trimethyl phosphate (*m/z* 141; 40% of the primary product ion distribution) and an ion of *m/z* 168 (60%) from transfer of ionized ethylene to trimethyl phosphate (Figure 2). The latter product was of special interest since this ion could be a distonic ion with no acidic functional groups or unsaturation near the charge site: $(CH_3O)_3P^+OCH_2CH_2^{\bullet}$.

The structure of the product ion of *m/z* 168 was investigated using collision-activated dissociation. This method involves kinetic excitation of the isolated ion which is then allowed to undergo energetic collisions with an inert target gas, usually argon. Collision-activated dissociation experiments are best carried out in the absence of molecules that could react with the excited ion or its ionic dissociation products. In order to avoid interference from ion-molecule reactions with the neutral reagents needed to produce the ion of *m/z* 168 (1,4-dioxane and trimethyl phosphate), these reagents were introduced into one side of the dual cell where the ion of *m/z* 168 was generated. After this, the ion was transferred into the other cell for collision-activated dissociation with argon.

An ion with the proposed structure $(CH_3O)_3P^+OCH_2CH_2^{\bullet}$ is expected to fragment by loss of a vinyl radical when activated, in analogy with the distonic isomer of ionized triethyl phosphate, $(CH_3CH_2O)_2P^+(OH)OCH_2CH_2^{\bullet}$ (Scheme III).[11] This is exactly what was observed (Figure 3a): formation of a fragment ion of *m/z* 141 by loss of $C_2H_3^{\bullet}$ dominates dissociation of the ion of *m/z* 168 at all collision energies used (15–75 eV, laboratory frame). The structure of the ion of *m/z* 141 generated in this fragmentation was investigated by isolating it and subjecting it to further collision-activated dissociation (an MS^3 experiment; see Scheme III). Dominant loss of methanol indicates that the structure of the ion of *m/z* 141 is likely to be that of protonated trimethyl phosphate. This was confirmed by the observation of similar fragmentation for protonated trimethyl phosphate[11] under the same conditions.

Scheme III



Scheme IV

The fragmentation patterns observed for the ion of *m/z* 168 strongly suggest that this ion has the structure proposed above: that of a phosphonium ion with an ethylene unit covalently bound to the phosphoryl oxygen.[14] Two findings indicate that the ion is not likely to be an electrostatically bound ion-molecule complex of ionized trimethyl phosphate and ethylene: (1) A phosphorus-oxygen bond can be cleaved in the ion of *m/z* 168 by collisional activation: the product ion of *m/z* 124 arises from loss of C_2H_4O (Figure 3a; Scheme III). (2) The reaction expected[1] to

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[10] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl. 1* **1988**, 17.

[11] Zeller, L.; Farrell, J.; Kenttämaa, H. I.; Vainiotalo, P. *J. Am. Chem. Soc.*, in press.

[12] Fraser-Monteiro, M. L.; Fraser-Monteiro, L.; Butler, J. J.; Baer, T.; Hass, J. R. *J. Phys. Chem.* **1982**, *86*, 739.

[13] Holmes, J. L.; Lossing, F. P. *Int. J. Mass Spectrom. Ion Processes* **1989**, *92*, 111.

[14] The structure $(CH_3O)_3P(OH)CH{=}CH_2^{\bullet +}$ can be ruled out on the basis of the following observations: loss of C_2H_4O upon collisional activation cannot occur for this ion; this ion is not expected to transfer ionized ethylene to nucleophiles; this ion is expected to undergo reactions characteristic of a conventional radical cation, e.g., a hydrogen atom abstraction with amines, and fast charge exchange with dimethyl disulfide (neither one of these reactions were observed); this ion is expected to exchange one of the hydrogen atoms (hydroxyl hydrogen) with deuterium when reacted with deuterated ammonia.

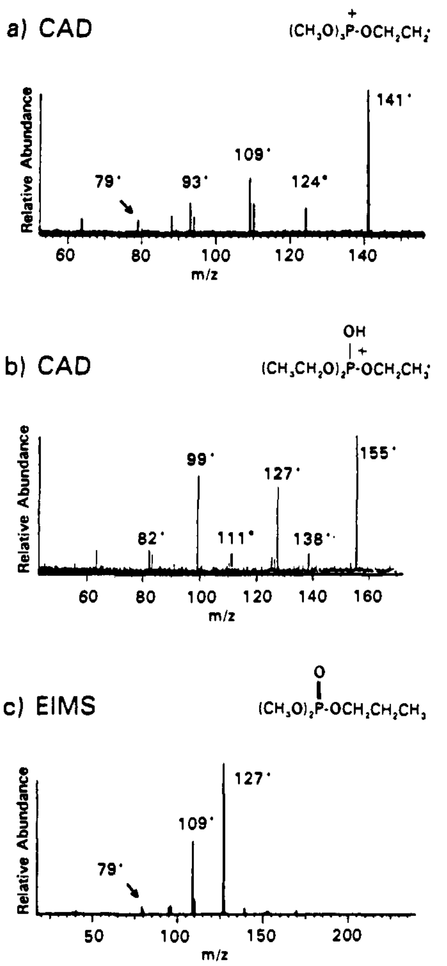


Figure 3. (a) Collision-activated dissociation products of the distonic ion of *m/z* 168 (35-eV collision energy, laboratory frame). (b) Collision-activated dissociation products of the distonic isomer of ionized triethyl phosphate (25-eV collision energy, laboratory frame). Loss of a vinyl radical to give $(CH_3CH_2O)_2P(OH)_2^+$ (*m/z* 155) dominates the fragmentation, and is followed by consecutive losses of one or two ethylenes to yield the ions of *m/z* 127 and 99, respectively. Loss of C_2H_4O yields the ion $(CH_3CH_2O)_2P(OH)^{\bullet+}$ (*m/z* 138). (c) 25-eV electron ionization mass spectrum of dimethyl propyl phosphate. Loss of $C_3H_5^{\bullet}$ to yield $(CH_3O)_2P(OH)_2^+$ (*m/z* 127) dominates the fragmentation. Loss of a propoxy radical yields the ion of *m/z* 109.

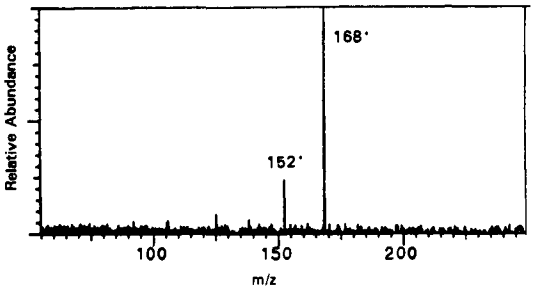
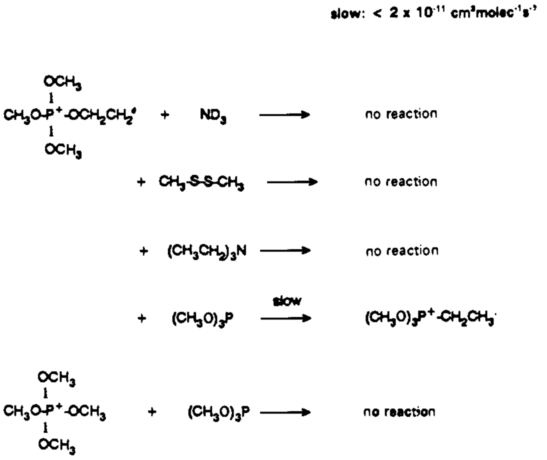


Figure 4. Reaction of the distonic organophosphorus ion of *m/z* 168 with trimethyl phosphite for 10 s (nominal pressure 1 × 10^{-7} Torr) resulting in slow transfer of ionized ethylene to trimethyl phosphite (to generate *m/z* 152). A small amount of protonated trimethyl phosphite (at *m/z* 125) is also observed.

Scheme V



dominate the dissociation of a loosely bound complex of ionized trimethyl phosphate and ethylene, formation of ionized trimethyl phosphate (*m/z* 140) and neutral ethylene, was not observed in any of the collisional activation experiments.

The distonic ion of *m/z* 168 is not in rapid equilibrium with other isomeric distonic forms via hydrogen atom transfer between the alkyl substituents (Scheme IV). This conclusion is based on several observations, including the fact that the fragmentation reaction indicative[11] of the isomerized ion structure $(CH_3O)_2P^+(OCH_2^{\bullet})OCH_2CH_3$, loss of formaldehyde, is not observed upon collisional activation of the ion of *m/z* 168. Further, the isomerized structure is expected to transfer ionized methylene to strong nucleophiles, in analogy[1] with other nonacidic distonic ions with the odd spin next to a heteroatom that formally carries part of the charge (e.g., $CH_2O^+CH_2^{\bullet}$). Although the ion of *m/z* 168 transfers ionized ethylene to certain nucleophiles (see discussion below), transfer of ionized methylene does not take place.

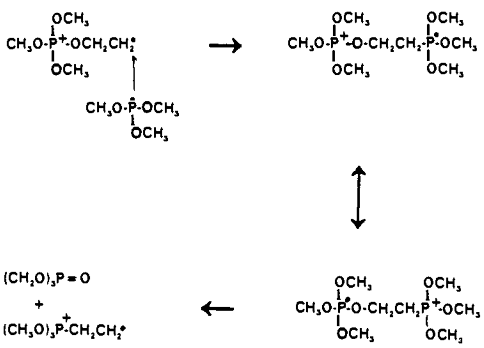
Examination of the reactions of the ion of *m/z* 168 with deuterated ammonia provides further support for the proposal that the ion does not have acidic functional groups near the charge site. Deuterated ammonia is known[11] to exchange all the hydroxyl hydrogens with deuterium atoms in even-electron phosphonium ions and in distonic isomers of ionized organophosphorus esters. However, no reactions were observed between the distonic ion of *m/z* 168 and deuterated ammonia even after a reaction time of 3 s (≥130 collisions with ND_3 at a nominal pressure of 3 × 10^{-7} Torr).

It should be noted here that the collision-activated dissociation products of the distonic ion of *m/z* 168 are qualitatively different from the dissociation products obtained for the conventional isomer, ionized dimethyl propyl phosphate. This molecular ion cannot be isolated for collisional activation studies since it is not thermodynamically stable;[11] instead, the electron ionization induced dissociation reactions of dimethyl propyl phosphate were investigated over a wide electron energy range (12–75 eV). Ionized dimethyl propyl phosphate predominantly fragments by loss of $C_3H_5^{\bullet}$ to yield a fragment ion of *m/z* 127 (Figure 3c) which contrasts the preference of its distonic isomer to lose $C_2H_3^{\bullet}$ and to generate an abundant ion of *m/z* 141 (Figure 3a).

Bimolecular Reactions of the Distonic Phosphonium Ion. Most organic radical cations undergo electron transfer if the reaction is exothermic. However, charge exchange does not take place for the distonic phosphonium ion of *m/z* 168 (Scheme V). The distonic ion does not react at all with CH_3SSCH_3 in spite of the fact that dissociative charge exchange yielding neutral trimethyl phosphate and ethylene is estimated to be exothermic by about 10 kcal/mol (Table I). The ion of *m/z* 168 undergoes a very slow reaction with the strong nucleophiles trimethyl phosphite and triethyl phosphite (k_{obs}/k_{ADO},[8] or the reaction efficiency, is less than 0.01; $k_{obs} \leq 1 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹; $k_{ADO} = 1.4 \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹). Transfer of ionized ethylene dominates for both reagents (in the case of trimethyl phosphite, to yield an ion of *m/z* 152; Scheme V, Figure 4). The origin of the product ion was verified by ejecting the phosphonium ion from the cell prior to the reaction period.

The observed transfer of ionized ethylene from the distonic phosphonium ion to phosphorus nucleophiles is not likely to occur by an S_N2 mechanism at the α-carbon since the ion does not transfer a methyl cation to any of the neutral reagents investigated.

Scheme VI



The transfer of $C_2H_4^{\bullet +}$ may involve a radical-type mechanism, perhaps via the hypervalent phosphorus radical intermediate depicted in Scheme VI. This proposal is supported by the results obtained for triethylamine and *sec*-butylamine that cannot generate an analogous intermediate radical: the distonic ion does not react at a measurable rate with these strong nucleophiles.

Conclusions

The reactivity of the first reported β-distonic radical cation that does not have acidic functional groups or unsaturation near the charge site differs from the behavior of most gaseous organic radical cations with a localized charge: no fast bimolecular reactions are observed for this ion. The fundamental reasons behind the observed resistance of this distonic ion to react with very strong bases, nucleophiles, and reductants are not clear at this time, although steric hindrance probably plays a role.[15] Electron transfer would be highly exothermic for some of the reagents studied but was not observed. Proton transfer dominates the chemistry of most known distonic radical cations.[1-4,11,12] However, deprotonation does not occur readily for the distonic phosphonium ion studied here although deprotonation through 1,2-elimination would be exothermic by 9 kcal/mol for the triethylamine base, and exothermic 1,2-eliminations are often fast in the gas phase.[16] It should be noted here that the limited amount of data available on *even-electron* phosphonium ion suggests that these ions are also quite unreactive in the gas phase. For example, it was observed during this study that methylated trimethyl phosphate, $(CH_3O)_4P^+$, does not react with trimethyl phosphite (Scheme V) in spite of the fact that methyl cation transfer from the ion to trimethyl phosphite is expected to be exothermic by 10 kcal/mol.[17]

The results presented here demonstrate that gaseous ions with spatially separated radical and charge sites can be quite unreactive in the gas phase. Thus far, high reactivity has only been observed[1-4,11,14] for those distonic ions that are Brönsted acids: these ions undergo fast deprotonation if the reaction is exothermic. It is concluded that *a spatially separated radical and charge site does not necessarily lead to high reactivity in gaseous radical cations*, and that *high reactivity may not be a general characteristic of distonic radical ions.*

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grant CHE-9107121), for partial support of this research.

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The Surface Chemistry of Vinyl Iodide on Pt(111)

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Abstract: Regardless of exposure, only submonolayer amounts of vinyl iodide (CH_2CHI) decompose, either during adsorption on Pt(111) at 100 K or during subsequent heating to 165 K. The remainder desorbs molecularly. The dissociation products are vinyl (CH_2CH) fragments, an important C_2 intermediate in hydrocarbon catalysis, and atomic iodine. Using the tools of surface science we have explored the formation and subsequent reactions of vinyl species in the presence of unavoidably coadsorbed atomic iodine. While some vinyl exists up to 450 K, there are two important and competitive lower temperature reaction channels which lead to ethylidyne (CCH_3) and ethylene (CH_2CH_2). From our results, we conclude that the rate of ethylidyne formation from adsorbed ethylene is controlled by the rate at which the first C–H bond in ethylene breaks, and in agreement with Zaera,[1,2] we find that vinyl is a facile intermediate in the process.

1. Introduction

Numerous experimental and theoretical studies have dealt with the chemisorption and reactions, particularly to form ethylidyne, of ethylene on Pt(111).[3-5] During heating from low temperatures, a strong hydrogen-desorption peak, which accompanies the decomposition of di-σ-bonded ethylene to form ethylidyne, is observed near 300 K. A second strong hydrogen-desorption peak, at 512 K, accompanies the conversion of ethylidyne to a polymonic hydrogen-deficient species.[4] Although the structures of ethylene and ethylidyne on Pt(111) have been well established, the mechanism of conversion from ethylene to ethylidyne remains controversial. Several intermediates, such as ethyl (CH_2CH_3),[6] vinyl ($CHCH_2$),[1,2] ethylidene ($CHCH_3$),[7] and vinylidene (CCH_2),[8] have been

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