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The Prototypical Organophosphorus Ylidion $^{\bullet}CH_2PH_3^+$

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Abstract: The reactivity of the prototypical phosphorus-containing ylidion (α-distonic ion) $^{\bullet}CH_2PH_3^+$ has been investigated in the gas phase by using a dual cell Fourier-transform ion cyclotron resonance mass spectrometer. The ion $^{\bullet}CH_2PH_3^+$ and its more stable conventional isomer $CH_3PH_2^{\bullet+}$ show distinctly different reactivities toward neutral reagents. This observation contrasts the facile interconversion of the analogous sulfur- and oxygen-containing distonic ions $^{\bullet}CH_2SH_2^+$ and $^{\bullet}CH_2OH_2^+$ with their conventional isomers $CH_3OH^{\bullet+}$ and $CH_3SH^{\bullet+}$, respectively, within collision complexes in the gas phase. Bracketing experiments yield a proton affinity of 190.4 ± 3 kcal mol^{-1} for the phosphorus atom in $^{\bullet}CH_2PH_2$. Together with a calculated heat of formation for $^{\bullet}CH_2PH_2$, this value yields a heat of formation of 217 ± 3 kcal mol^{-1} (at 298 K) for the distonic ion $^{\bullet}CH_2PH_3^+$.

Introduction

Distonic radical cations[1] (ionized ylides, zwitterions, and biradicals) have been the focus of numerous recent experimental gas-phase studies and theoretical investigations.[2] However, examination of the reactivity of distonic ions containing second-row elements is currently limited to some distonic isomers of trimethyl and triethyl phosphate radical cations,[3] i.e., the ions $^{\bullet}CH_2OP^+(OH)(OCH_3)_2$ and $^{\bullet}CH_2CH_2OP^+(OH)(OCH_2CH_3)_2$, and the ions $^{\bullet}CH_2CH_2OP^+(OCH_3)_3$,[4] $^{\bullet}CH_2S^+(CH_3)_2$,[5] and $^{\bullet}CH_2SH_2^+$.[6]

The prototypical α-distonic ions or ylidions containing second-row elements (*e.g.*, $^{\bullet}CH_2PH_3^+$ and $^{\bullet}CH_2SH_2^+$) are of special interest since the knowledge concerning their properties provides the basis for the understanding of more complex second-row distonic ions. A recent study[6] on the gas-phase reactions of $^{\bullet}CH_2SH_2^+$ in a Fourier-transform ion cyclotron resonance (FT/ICR) mass spectrometer revealed interesting reactivity that is quite different from that reported[7] for the oxygen-containing ylidion $^{\bullet}CH_2OH_2^+$. The latter ion reacts predominantly by proton transfer and hydrogen atom abstraction.[7] Moreover, it shows reactivity virtually identical to that of $CH_3OH^{\bullet+}$ toward neutral molecules whose proton affinities are greater than that of $^{\bullet}CH_2OH$ (166 kcal mol^{-1}),[7] likely because of interconversion of $^{\bullet}CH_2OH_2^+$ and $CH_3OH^{\bullet+}$ *via* intramolecular 1,2-hydrogen migration catalyzed by the neutral reagent.[7] In contrast, $^{\bullet}CH_2SH_2^+$ reacts with many neutral reagents by electron abstraction. This reaction is thought[6] to occur by a stepwise mechanism involving proton transfer from the ion to the neutral reagent molecule, followed by hydrogen atom transfer or proton transfer accompanied by electron transfer within the collision complex. Further, compounds with ionization energies greater than 9.9 eV and proton affinities greater than 180 kcal mol^{-1} were found to induce base-catalyzed isomerization of the ylidion $^{\bullet}CH_2SH_2^+$ to the more stable conventional isomer $CH_3SH^{\bullet+}$.[6] These results are in keeping with the theoretical prediction that second-row distonic ions with a carbon radical center are generally less stable than their conventional counterparts.[8]

The prototypical phosphorus-containing ylidion $^{\bullet}CH_2PH_3^+$ has been generated by electron ionization-induced McLafferty rearrangement of *n*-hexylphosphine (Scheme 1), and structurally characterized by collision-activated dissociation (CAD).[9] The CAD spectrum of $^{\bullet}CH_2PH_3^+$ features intense structurally diagnostic fragment ion peaks at *m/z* 34 ($PH_3^{\bullet+}$) and *m/z* 14 ($CH_2^{\bullet+}$). In contrast, the dissociation product distribution obtained upon collisional activation of $CH_3PH_2^{\bullet+}$ (generated by electron ionization of methylphosphine) yields abundant signals at *m/z* 15 (CH_3^+) and *m/z* 33 (PH_2^+).[9] Further, neutralization−reionization experiments involving $^{\bullet}CH_2PH_3^+$ have demonstrated that this ion has a lifetime of at least several microseconds and that it is a suitable precursor for the generation of the hitherto

Scheme 1

$$CH_3(CH_2)_4CH_2PH_2 \xrightarrow[\text{impact}]{\text{electron}} CH_3(CH_2)_4CH_2PH_2^{\bullet+} \xrightarrow[-C_5H_{10}]{} {}^{\bullet}CH_2PH_3^+$$

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unknown neutral ylide $CH_2{=}PH_3$ (methylenephosphorane).[10] These experimental findings support a theoretical prediction that the distonic and conventional $CH_5P^{\bullet +}$ radical cations correspond to minima on the potential energy surface. The ion $CH_3PH_2^{\bullet +}$ has been calculated to be 8 kcal mol^{-1} more stable than $^{\bullet}CH_2PH_3^+$ (at the QCISD/6-311+G(3df,2p)//MP2/6-311+G(2df,p) level of theory)[8c] and to be separated from the latter ion by a barrier of 52.6 kcal mol^{-1} (at the UMP3/6-31G(d,p)//6-31G(d,p) level of theory).[8b]

We report here the first systematic study of the intrinsic chemical properties of the prototypical phosphorus-containing ylidion $^{\bullet}CH_2PH_3^+$. The ion $^{\bullet}CH_2PH_3^+$ was found to have very different chemical properties from those of $CH_3PH_2^{\bullet +}$ and hence to be stable toward isomerization. The proton affinity of the phosphorus atom in $^{\bullet}CH_2PH_2$ was experimentally determined to be 190.4 ± 3 kcal mol^{-1}. This value, combined with a calculated heat of formation for $^{\bullet}CH_2PH_2$, yields a heat of formation of 217 ± 3 kcal mol^{-1} for $^{\bullet}CH_2PH_3^+$.

Experimental Section

All experiments were conducted utilizing a Model 2001 Extrel Fourier transform ion cyclotron resonance mass spectrometer that has been described elsewhere.[3,11] The instrument consists of a dual cell (two 4.7 cm cubic cells) that is aligned collinearly with the magnetic field produced by a 3 T superconducting magnet operated at 2.2−2.8 T. The dual cell is differentially pumped to a nominal base pressure of less than 10^{-9} Torr by using two Balzers turbomolecular pumps (330 L s^{-1}), each backed with an Alcatel 2012 mechanical pump. A typical experiment consisted of five steps: ion formation in one cell, transfer of the ions into the other cell, collisional cooling, isolation of the desired ion, and detection after a variable reaction time.

The ion $^{\bullet}CH_2PH_3^+$ was generated by electron ionization of *n*-hexylphosphine added into the instrument with a heated batch inlet system equipped with a leak valve. $CH_3PH_2^{\bullet +}$ was generated by electron ionization of $CH_3PH_2{\bullet}HI$ that was introduced into the system with a heated solids probe. The nominal pressure was typically 1×10^{-7} Torr in the cell wherein the ions were generated. The ion signal was optimized by varying the ionization energy (20−70 eV), the ionization time (20−50 ms), and the emission current (4−8 μA). At all times except during unselective ejection of unwanted ions prior to ion transfer and during ion transfer, the ions were trapped in the center of one side of the dual cell by applying +2.0 V potential onto the plates perpendicular to the magnetic field (trapping plates). Ions were transferred between the two sides of the dual cell through a 2 mm hole in the middle plate (conductance limit) by grounding this plate for 100−200 μs. Ions were kinetically and internally cooled by multiple collisions with argon atoms pulsed[12] into the cell at a peak nominal pressure of 1×10^{-5} Torr. The ion of interest was isolated by using the stored waveform inverse Fourier transform method[13] (with an Extrel SWIFT module) to generate rf pulses that ejected all undesired ions from the cell. The isolated ion was allowed to undergo reactions for variable time intervals with neutral reagents introduced into the cell at a nominal pressure of 1×10^{-7} Torr. Detection of ions was achieved by exciting all the ions present in the cell into larger orbits through the use of a radio frequency sweep ("chirp") of 124 V_{p-p} amplitude and a 3.2 kHz μs^{-1} sweep rate. The spectra were recorded as 32k data points subjected to one zero fill prior to Fourier transformation.

All reagents, with the exception of methyl- and *n*-hexylphosphines, were commercially obtained and used as received except dimethyl diselenide which was vacuum distilled. Their purity was verified by mass spectrometry. *n*-Hexylphosphine and methylphosphine were synthesized by established procedures.[14] The solid adduct $CH_3PH_2{\bullet}HI$ was generated[15] by adding dry HI gas to frozen CH_3PH_2, which was maintained at −196 °C. The gaseous HI was generated by adding a water solution of HI dropwise into P_4O_{10}.

The reaction rate constants (k_{exp}) were obtained from the slope of the plot of the natural logarithm of the relative abundance of the reactant ion as a function of reaction time. Collision rate constants (k_{coll}) were calculated using the parametrized trajectory theory.[16] The reaction efficiency is given by k_{exp}/k_{coll}. For rate measurements, the ion gauges were calibrated for their sensitivity[17] toward the neutral reagent. Correction for the pressure gradient between the ion gauge and the dual cell was obtained by measuring rates of reactions with known rate constants involving each neutral reagent. The branching ratios of competitive reaction channels were derived from constant relative abundances of the product ions measured at short reaction times.

The *ab initio* molecular orbital calculations were carried out utilizing the Gaussian 92 suite of programs[18] on a Convex C220 supercomputer at the University of Düsseldorf. Geometry optimizations of stationary points were executed at the UMP2(FU)/6-311+G(2df,p) level of theory by using the analytical gradient technique (Berny optimization).[19−21] Vibrational frequencies were calculated at the UMP2(FU)/6-311+G(2df,p)//UMP2(FU)/6-311+G(2df,p) level of theory in order to obtain zero point energies (scaled by 0.9) and to ensure that the optimized structures were true minima on the potential energy surfaces. The spin contamination, as expressed by $\langle S^2 \rangle$, was found to be within an acceptable range (0.763−0.772) for all the structures examined ($\langle S^2 \rangle = 0.75$ for the pure spin state).

Results and Discussion

Intrinsic Chemical Properties of $^{\bullet}CH_2PH_3^+$ and $CH_3PH_2^{\bullet +}$. Examination of the gas-phase reactivity of the distonic ion $^{\bullet}CH_2PH_3^+$ and its conventional isomer $CH_3PH_2^{\bullet +}$ reveals that these ions are distinct species: the two ions possess very different chemical properties. Radical-type abstraction reactions and proton transfer reactions dominate for $^{\bullet}CH_2PH_3^+$ (Table 1). In sharp contrast, $CH_3PH_2^{\bullet +}$ reacts by predominant electron abstraction with most of the reagents studied (Table 1). All the reactions examined were found to follow pseudo-first-order kinetics (for example, see Figures 1 and 2). This finding further supports the conclusion that $^{\bullet}CH_2PH_3^+$ and $CH_3PH_2^{\bullet +}$ do not isomerize within the collision complexes involving the neutral reagent molecules studied. The reactivity of the isomeric ions is discussed in detail below.

The reagents CH_3SSCH_3 and $CH_3SeSeCH_3$ commonly react with distonic ions by transfer of $CH_3S^{\bullet}$ and $CH_3Se^{\bullet}$, respectively.[2bd,22,24,25] Indeed, $CH_3S^{\bullet}$ abstraction was observed upon reaction of $^{\bullet}CH_2PH_3$ with CH_3SSCH_3 (the elemental composition of the product ion was verified by an accurate mass

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Table 1. Reactions of $^{\bullet}CH_2PH_3^+$ and $CH_3PH_2^{\bullet+}$ with Selected Neutral Reagents

		reactions of $^{\bullet}CH_2PH_3^+$		reactions of $CH_3PH_2^{\bullet+}$	
reagent	IE[a] (eV)	products (%)	efficiency[e]	products (%)	efficiency[e]
dimethyl disulfide	8.1[b]	$CH_3SSCH_3^{\bullet+}$ (50) $CH_3SCH_2PH_3^+$ (50)	0.4	$CH_3SSCH_3^{\bullet+}$	≃1.2
dimethyl diselenide	7.9[c]	$CH_3SeCH_2PH_3^+$	0.7	$CH_3SeSeCH_3^{\bullet+}$	0.7
allyl iodide	9.3	CH_5IP^+	0.3	CH_5IP^+	1.0
benzeneselenol	8.3[d]	$CH_3PH_3^+$	*g*	$C_6H_5SeH^{\bullet+}$ (100)	*g*
acetaldehyde	10.2	no reaction		$CH_3PH_3^+$	0.3
triethylamine	7.5	$(CH_3CH_2)_3NH^+$ [f] $(CH_3CH_2)_3N^{\bullet+}$ (48) $(CH_3CH_2)_2N{=}CH_2^+$ (52)	1.3	$(CH_3CH_2)_3N^{\bullet+}$ (73) $(CH_3CH_2)_2N{=}CH_2^+$ (27)	1.3

[a] Values taken from ref 20a unless otherwise noted. [b] Value taken from ref 21. [c] Value taken from ref 22. [d] Value taken from ref 23. [e] k_{exp}/k_{coll}. [f] This is a major secondary product; some of these ions may also be formed as a primary product. [g] Not measured.

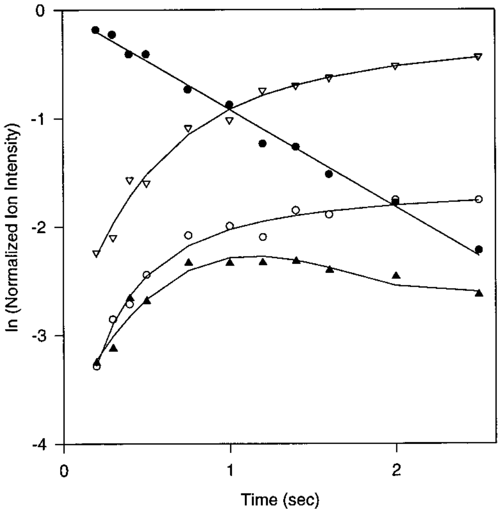

Figure 1. Temporal variation of the abundances of the reactant ion $^{\bullet}CH_2PH_3^+$ (*m/z* 48, ●) and the product ions $(CH_3CH_2)_3N^{\bullet+}$ (*m/z* 101, ▲), $(CH_3CH_2)_2N{=}CH_2^+$ (*m/z* 86, ○), and $(CH_3CH_2)_3NH^+$ (*m/z* 102, ▽) upon reaction with $(CH_3CH_2)_3N$. The lines are arbitrary smooth curves drawn through the data points.

measurement. However, the reaction is accompanied by electron abstraction. $CH_3SeSeCH_3$ is more reactive toward organic radical cations than CH_3SSCH_3 and often reacts by exclusive $CH_3Se^{\bullet}$ transfer.[22,25] Also $^{\bullet}CH_2PH_3^+$ reacts with $CH_3SeSeCH_3$ by exclusive $CH_3Se^{\bullet}$ abstraction (Table 1). In sharp contrast, the only reaction channel observed for the conventional radical cation $CH_3PH_2^{\bullet+}$ with both of these neutral reagents is electron transfer (Table 1). This result is in keeping with the earlier findings that most known conventional radical cations react with CH_3SSCH_3 and $CH_3SeSeCH_3$ by exclusive electron abstraction if the reaction is exothermic.[2b]

The isomeric ions show different reactivity toward most of the neutral reagents studied. The efficient hydrogen atom donor C_6H_5SeH readily transfers a hydrogen atom to $^{\bullet}CH_2PH_3^+$, in analogy with the observations made earlier for other distonic ions.[5b] In contrast, the conventional radical cation $CH_3PH_2^{\bullet+}$ reacts by electron abstraction (Table 1). The distonic ion is unreactive toward CH_3CHO while the conventional ion $CH_3PH_2^{\bullet+}$ abstracts a hydrogen atom from this reagent.

Many distonic ions have been reported[5b] to abstract $CH_2{=}CHCH_2^{\bullet}$ and/or $I^{\bullet}$ from $CH_2{=}CHCH_2I$. In keeping with these findings, $I^{\bullet}$ abstraction was observed when $^{\bullet}CH_2PH_3^+$ was allowed to react with $CH_2{=}CHCH_2I$. In this case, the same reaction was observed for $CH_3PH_2^{\bullet+}$. This result was not unexpected since some conventional radical cations are known to abstract $I^{\bullet}$ from allyl iodide.[5b]

Proton Transfer Reactions. The proton affinity of the phosphorus atom in $^{\bullet}CH_2PH_2$ was experimentally determined by reacting $^{\bullet}CH_2PH_3^+$ with a series of neutral compounds with known proton affinities and monitoring the occurrence of proton transfer (Table 2). Given that proton transfer occurs from $^{\bullet}CH_2PH_3^+$ to propionic acid and 2-propanol (proton affinities 191.8 and 191.2 kcal mol^{-1}, respectively) but not to propionaldehyde (proton affinity 189.6 kcal mol^{-1}), the proton affinity of $^{\bullet}CH_2PH_3^+$ at the phosphorus atom is concluded to be 190.4 ± 3 kcal mol^{-1}.

$\Delta H_f(^{\bullet}CH_2PH_3^+)$ can be derived from the proton affinity of the phosphorus atom in the radical $^{\bullet}CH_2PH_2$ and the heats of formation for $^{\bullet}CH_2PH_2$ and H^+ (Scheme 2). Since $\Delta H_f(^{\bullet}CH_2PH_2)$ is not known, an estimate for this value was obtained by using the isodesmic reaction shown in Scheme 3. At the UMP2(FU)/6-311+G(2df,p) level of theory (including ZPVE correction), the enthalpy change of the isodesmic process was calculated to be 5.0 kcal mol^{-1} (at 0 K). Using the known[20a,b] experimental heats of formation (ΔH_f^{298}) of CH_3PH_2, CH_4, and $CH_3^{\bullet}$, $\Delta H_f^{298}(^{\bullet}CH_2PH_2)$ was concluded to be 42.2 kcal mol^{-1} (Table 3). Together with the experimentally determined proton affinity of the phosphorus atom in $^{\bullet}CH_2PH_2$, this value yields $\Delta H_f^{298}(^{\bullet}CH_2PH_3^+)$ = 217 ± 3 kcal mol^{-1}. This value is somewhat greater than an earlier computational prediction of 212 kcal mol^{-1} (G2′ method).[8c]

Scheme 2

$$^{\bullet}CH_2PH_3^{\ +} \rightarrow {}^{\bullet}CH_2PH_2 + H^+ \qquad \Delta H_{reactn} = PA$$

$$\Delta H_f(^{\bullet}CH_2PH_3^{\ +}) = \Delta H_f(^{\bullet}CH_2PH_2) + \Delta H_f(H^+) - PA$$

Scheme 3

$$^{\bullet}CH_2PH_2 + CH_4 \xrightarrow{\Delta H_{reactn}} CH_3PH_2 + {}^{\bullet}CH_3$$

$$\Delta H_f(^{\bullet}CH_2PH_2) = \Delta H_f(CH_3PH_2) + \Delta H_f(^{\bullet}CH_3) - \Delta H_f(CH_4) - \Delta H_{reactn}$$

Electron Transfer Reactions. The reactions of $^{\bullet}CH_2PH_3^+$ with $(C_2H_5)_3N$ and CH_3SSCH_3, yield abundant electron transfer products. These reactions are not likely to occur via simple electron transfer to yield $CH_2{=}PH_3$ (calculated ionization energy

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Table 2. Reactions between $^{\bullet}CH_2PH_3^+$ and Neutral Reagents with Known Proton Affinities (PA) and Ionization Energies (IE)

reagent	PA[a] (kcal mol^{-1})	IE[a] (eV)	reaction
benzaldehyde	200.2	9.4	predominant proton transfer
2-butanol	195	9.88	proton transfer
2-methyl-2-propanol	193.7	9.90	proton transfer
propionic acid	191.8	10.53	proton transfer
2-propanol	191.2	10.12	proton transfer
propionaldehyde	189.6	10.23	no reaction
acetaldehyde	186.6	10.2	no reaction
methanol	181.9	10.82	no reaction

[a] Values taken from ref 20a. [b] Value taken from ref 21.

Table 3. Calculated Total Energies (hartrees) and Experimental Heats of Formation (ΔH_f^{298}) of the Species Used To Calculate $\Delta H_f^{298}(^{\bullet}CH_2PH_2)$

species	energy[a] (hartrees)	ΔH_f^{298} (kcal mol^{-1})	species	energy[a] (hartrees)	ΔH_f^{298} (kcal mol^{-1})
$^{\bullet}CH_3$	−39.718 06	35.0[b]	CH_3PH_2	−381.965 41	−4.0[c]
CH_4	−40.377 47	−16.2[b]	$^{\bullet}CH_2PH_2$	−381.313 99	42.2[d]

[a] UMP2-Full/6-31+G(2df,p) + ZPVE (scaled by 0.9). [b] Value taken from ref 20b. [c] Value taken from ref 20a. [d] Obtained in this work using the equation in Scheme 3 and the other values shown in this table.

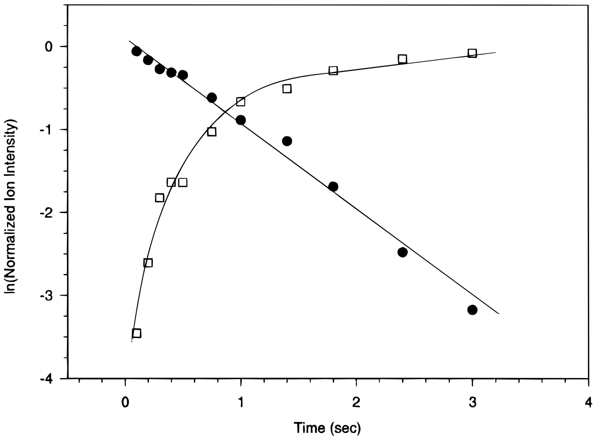
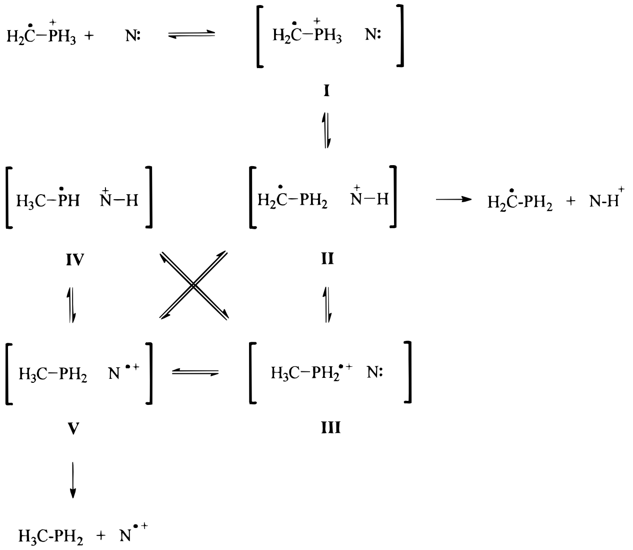


Figure 2. Temporal variation of the abundances of the reactant ion $^{\bullet}CH_2PH_3^+$ (*m/z* 48, ●) and the product ion $CH_3PH_3^+$ (*m/z* 49, □) upon reaction with C_6H_5SeH. The lines are arbitrary smooth curves drawn through the data points.

6.8 eV) since this process would be highly endothermic.[8b] An intramolecular 1,2-hydrogen shift in $^{\bullet}CH_2PH_3^+$ to yield the more stable conventional isomer $CH_3PH_2^{\bullet+}$ *prior to* reaction with the above neutral reagents would explain the observed reactivity, since $CH_3PH_2^{\bullet+}$ was found to react by predominant electron abstraction with these neutral reagents. However, the results discussed above rule out this isomerization. Furthermore, *ab initio* molecular orbital calculations carried out[8b] at the UMP3/6-31G(d,p) level of theory predict that $^{\bullet}CH_2PH_3^+$ is separated from $CH_3PH_2^{\bullet+}$ by a very high barrier (43 kcal mol^{-1}).[8b] A barrier of this size cannot be overcome even when assisted by the ion−dipole energy of an ion−molecule collision complex (typically in the range of 10−20 kcal mol^{-1}). Partial isomerization is experimentally ruled out on the basis of the finding that the decay of the natural logarithm of the signal of $^{\bullet}CH_2PH_3^+$ as a function of time follows the expected pseudo-first-order kinetics for all the reactions studied, as exemplified by the reaction of $^{\bullet}CH_2PH_3^+$ with triethylamine in Figure 1 and with benzeneselenol in Figure 2. These observations strongly suggest that the ion population does not consist of mixtures of isomeric ions. Further support for this conclusion comes from the different reaction rates of $^{\bullet}CH_2PH_3^+$ and $CH_3PH_2^{+\bullet}$, for example, toward CH_3SSCH_3 and $CH_2{=}CHCH_2I$ (Table 1).

Scheme 4



The electron transfer reactions observed for $^{\bullet}CH_2PH_3^+$ can be readily explained on the basis of the recently proposed "shuttle" mechanism.[26] The same mechanism was used to rationalize the electron transfer reactions involving the ion $^{\bullet}CH_2SH_2^+$.[6] This mechanism involves an initial proton transfer between the ion and the neutral reagent. If the reaction is highly exothermic, the resulting complex **II** (Scheme 4) may decompose. Alternatively, hydrogen atom transfer may occur to the carbon radical site in $^{\bullet}CH_2PH_2$, generating the complex **V** that consists of neutral CH_3PH_2 and the radical cation of the reagent. Decomposition of this complex yields the observed electron transfer product. Another possible reaction channel involves proton transfer within complex **II**, yielding complex **III**. Since the recombination energy of $CH_3PH_2^{\bullet+}$ (9.12 eV)[20a] is greater than the ionization energies of the reagents of interest (($(CH_3CH_2)_3N$, 7.5 eV;[20a] CH_3SSCH_3, 8.1 eV[21]), electron transfer within complex **III** is likely to occur readily to produce complex **V** that then decomposes to yield the electron transfer product (**III** to **IV** transition is also posible but less likely).

Most of the reactions of the sulfur-containing distonic ion $^{\bullet}CH_2SH_2^+$ are dominated by electron transfer and indistinguishable from those of its conventional isomer $CH_3SH^{\bullet+}$.[6] In contrast, $^{\bullet}CH_2PH_3^+$ shows reactivity distinctly different from that of $CH_3PH_2^{+\bullet}$. This is likely explained by several facts. First, $^{\bullet}CH_2SH_2^+$ is significantly more acidic ($PA(^{\bullet}CH_2SH) \leq 176$ kcal mol^{-1} at S) than $^{\bullet}CH_2PH_3^+$ ($PA(^{\bullet}CH_2PH_2) = 190$ kcal mol^{-1} at P) and hence more easily deprotonated within a collision complex with a base. Second, the driving force for isomerization of $^{\bullet}CH_2SH_2^+$ to the conventional isomer is calculated to be −19 kcal mol^{-1}, while that for $CH_3PH_2^{\bullet+}$ is only −11 kcal mol^{-1} (Table 4).[8b] Finally, $^{\bullet}CH_2SH$ has a significantly greater dipole moment (1.3 D) than $^{\bullet}CH_2PH_2$ (0.9 D; both values were calculated at the UHF/3-21G(d) level of theory; Table 5). Hence, solvation of a protonated base BH^+ by $^{\bullet}CH_2SH$ within the collision complex is more efficient than by $^{\bullet}CH_2PH_2$. This results in a deeper well and a longer lifetime for the collision complex corresponding to BH^+ and $^{\bullet}CH_2SH$, making further reactions within this collision complex more likely.

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(26) Reddy, A. C.; Danovich, D.; Ioffe, A.; Shaik, S. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1525−1539.

Table 4. Calculated (G2′) and Experimental Heats of Formation (ΔH_f^{298}) for $CH_5P^{\bullet+}$ and $CH_4S^{\bullet+}$

	ΔH_f^{298} (kcal mol^{-1})			ΔH_f^{298} (kcal mol^{-1})	
ion	calcd[a]	exptl	ion	calcd[a]	exptl
$^{\bullet}CH_2PH_3^+$	212	217[b]	$^{\bullet}CH_2SH_2^+$	232	≥227[d]
$CH_3PH_2^{\bullet+}$	204	206[c]	$CH_3SH^{\bullet+}$	213	211[c]

[a] Value taken from ref 8c. [b] This work. [c] Value taken from ref 20a. [d] Value taken from ref 6.

Table 5. Calculated Dipole Moments of $^{\bullet}CH_2PH_2$ and $^{\bullet}CH_2SH$ (UHF/3-21G* Level of Theory)

species	*D*
$^{\bullet}CH_2PH_2$	0.8728
$^{\bullet}CH_2SH$	1.3173

Conclusion

The work described here represents the first study on the reactivity of the prototypical phosphorus-containing distonic ion $^{\bullet}CH_2PH_3^+$. The distinct reactivity of $^{\bullet}CH_2PH_3^+$ and that of its conventional isomer $CH_3PH_2^{\bullet+}$ demonstrate that these isomeric ions are stable, noninterconverting species. *This finding contrasts the recent suggestion*[7b] *that the interconversion of α-distonic ions and their conventional isomers within collision complexes of neutral reagents is a widespread phenomenon.* The conventional ion $CH_3PH_2^{\bullet+}$ reacts by predominant electron abstraction with most of the neutral molecules studied. In contrast, $^{\bullet}CH_2PH_3^+$ shows a variety of reactions, including proton transfer, atom abstraction, and group abstraction reactions. The proton affinity of the phosphorus atom in $^{\bullet}CH_2PH_2$ was determined to be 190 ± 3 kcal mol^{-1}. This value, together with a calculated heat of formation for $^{\bullet}CH_2PH_2$, yields an estimate of 217 ± 3 kcal mol^{-1} for the heat of formation of the distonic ion $^{\bullet}CH_2PH_3^+$.

The ion $^{\bullet}CH_2PH_3^+$ was found to react with $(C_2H_5)_3N$ and CH_3SSCH_3 to yield electron transfer products. These reactions are proposed to take place via a shuttle mechanism[26] that involves consecutive proton and either hydrogen or proton and electron transfers within the collision complex. This mechanism is in keeping with that recently reported[6] for the reactions of the sulfur-containing distonic ion $^{\bullet}CH_2SH_2^+$. The shuttle mechanism seems to constitute a general alternative for the traditional direct electron transfer mechanism for small organic ions.

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