

Mechanism of CH_2^+ Transfer from Distonic Ions $\text{X}-\text{CH}_2^+$ ($\text{X} = \text{CH}_2\text{O}$, CH_2CH_2) to π - and n -Electron Bases in the Gas Phase. A Fourier Transform Ion Cyclotron Resonance (FTICR) Study Supplemented by *ab initio* MO Calculations

Ridwan D. Rusli and Helmut Schwarz*

Institut für Organische Chemie, Technische Universität Berlin,
Straße des 17. Juni 135, D-1000 Berlin 12

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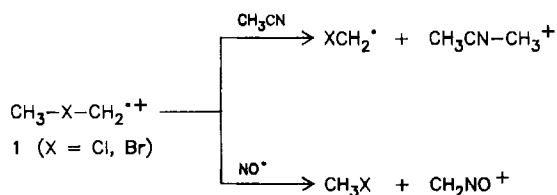
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The reactions of acetonitrile, propyne, acetylene, trimethylsilylacetylene, and tetramethylsilane, with distonic ions $\text{CH}_2\text{XCH}_2^+$ [$\text{X} = \text{CH}_2$ (**2**), O (**3**)] are studied in the gas phase using Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometry. In line with previous studies, CH_2^+ is transferred to the electron lone-pair of the nitrogen atom of CH_3CN to generate $\text{CH}_3\text{CN}-\text{CH}_2^+$ (**4**); upon collisional excitation, this ion undergoes competitive losses of H^+ and CH^+ . While both neutrals originate from the "methylene" unit of **4**, detailed studies employing labeled substrates and using various types of collision experiments reveal an intriguing dissociation pattern in that the dissociations are preceded by two intramolecular hydrogen migrations giving rise to $\text{CH}_3\text{C}(\text{H})=\text{NCH}^+$ (**6**) and $\text{CH}_3\text{C}=\text{N}(\text{H})\text{CH}^+$ (**7**). While **6** serves as intermediate en route to loss of H^+ from the "CH" moiety, **7** is the actual precursor to generate, by loss of CH^+ , protonated acetonitrile, CH_3CNH^+ (**12**) (Scheme 5). In addition, **12** is formed by bimolecular proton transfer. In this reaction, translationally excited $\text{CX}_3\text{CN}-\text{CY}_2^{+\bullet}$ ($\text{X}, \text{Y} = \text{H}, \text{D}$) transfers X^+ to neutral CX_3CN to generate CX_3CNX^+ (Scheme 4). The bimolecular proton transfer as well as the in-

tramolecular isomerizations of **4** to **6** and **7** are subject to very large kinetic isotope effects. In the transfer of CH_2^+ to $\text{CH}_3\text{C}\equiv\text{CH}$ two products are formed [i.e. $\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{CH}_3^+$ (**16**) and $\text{CH}_2=\text{C}=\text{CHCH}_3^+$ (**17**) presumably via intermediate **18** (Scheme 6)]; the latter is formed by addition of CH_2^+ to the less hindered carbon atom of $\text{HC}\equiv\text{CCH}_3$ reflecting the higher stability of the so-formed intermediate compared with addition to C-2. Reactions of **2** and **3** with $\text{HC}\equiv\text{CH}$ do not result in the formation of a detectable CH_2^+ -transfer product. When using $\text{CH}_2\text{CH}_2\text{CH}_2^+$ (**2**) the reaction is prohibited by the endothermicity to generate the initial complex (structurally related to **18**). On the other hand, when $\text{CH}_2\text{OCH}_2^+$ (**3**) is employed, the intermediate of CH_2^+ transfer is formed with sufficient energy to split off a hydrogen atom. Preliminary experiments with silicon-containing molecules, like $\text{Si}(\text{CH}_3)_4$ or $\text{HC}\equiv\text{CSi}(\text{CH}_3)_3$, demonstrate that the favored processes of these neutrals with **2** and **3** are due to charge transfer (in the form of an electron or an anion like CH_3^- or C_2H^-) from the silicon-containing molecule to the distonic ions. The experimental results obtained for the $\text{CH}_3\text{CN}/\text{CH}_2^+$ system are supported by *ab initio* MO calculations (3-21G/3-21G + ZPVE).

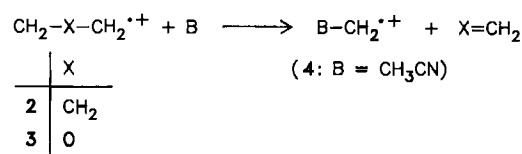
The increasing importance of distonic radical ions¹⁾ – species in which the charge and radical centres are formally separated – as central intermediates in both unimolecular and bimolecular reactions is well documented in several review articles²⁾. Among the conspicuous properties of these radical ions, their reactivity with electrophiles and nucleophiles in the gas phase is worth mentioning. For example, the radical cations **1** ($\text{X} = \text{Cl}, \text{Br}$) undergo with nucleophiles like CH_3CN specific transfer of a methyl cation, while with the electrophilic NO^+ the major reaction is due to transfer of a methylene radical cation (Scheme 1)³⁾.

Scheme 1



Transfer of CH_2^+ to basic molecules **B**, like NH_3 , PH_3 , and RCN , under the conditions of ion cyclotron resonance (ICR) mass spectrometry was also reported for the distonic ions $\text{CH}_2\text{CH}_2\text{CH}_2^+$ (**2**) and $\text{CH}_2\text{OCH}_2^+$ (**3**) formed from a variety of precursors (Scheme 2)⁴⁾. The ring-opened oxirane radical cation **3** also transfers CH_2^+ to other bases (like pyridine) and to unsaturated compounds^{4b-d,g,5)}.

Scheme 2



Since the heat of reaction, ΔH_r^0 , for the CH_2^+ transfer from **2** (**3**) is given by eq. (1) it follows that, for a given base **B**, the process may be controlled by choosing either **2** or **3** as the "transfer" reagent. By using the known heats of for-

mation of **2**, **3**, and $X = \text{CH}_2$ ($X = \text{CH}_2, \text{O}$), respectively, it can be shown that CH_2^+ transfer is 26 kcal/mol more exothermic for **3** compared with **2**. This, in principle, provides one with a handle to generate intermediates having enough internal energy to isomerize to energy-rich isomers and/or to decompose.

$$\Delta H_r^0 = \Delta H^0(\text{BCH}_2^+) + \Delta H_f^0(X = \text{CH}_2) - \Delta H_f^0(\text{B}) - \Delta H_f^0(\text{2,3}) \quad (1)$$

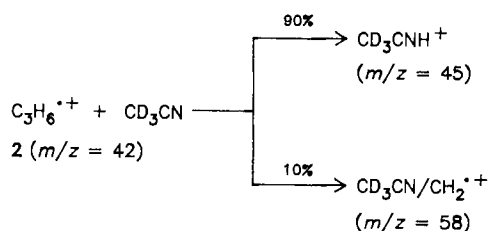
A considerable number of studies of the bimolecular reactions of distonic ions have described CH_2^+ transfer to acetonitrile, CH_3CN , as the base **B** (Scheme 2). The product ion is presumably the distonic ion $\text{CH}_3\text{CNCH}_2^+$ (**4**), but – as stated by Hammerum^{2d}) in his excellent review – the structure of this and similar species has not yet been examined in detail. In particular, no attention has been paid to alternative reactions, including insertion of CH_2^{++} into C–H and/or C–C bonds⁶) or isomerization processes following the initial addition of CH_2^+ to the nitrogen electron lone pair. The present paper⁷) aims at exploring these possibilities for the reactions of **2** and **3** with several bases **B** in the gas phase using Fourier Transform Ion Cyclotron Resonance (FTICR). The experimental results are supported by ab initio molecular orbital (MO) studies.

Results and Discussion

A) Reactions of $\text{CH}_2\text{XCH}_2^+$ (**2**, **3**) with CH_3CN

When $\text{CH}_2\text{CH}_2\text{CH}_2^+$ (**2**), generated by 70-eV ionization of cyclopropane, is treated for 3 s with CD_3CN ⁸) at a constant acetonitrile pressure of 2.5×10^{-8} mbar, the product distribution shown in Scheme 3 is obtained. Variations of either reaction time or pressure have minor effects on the branching ratio for H^+ versus CH_2^+ transfer. Double-resonance experiments confirm that both products originate from the $\text{CD}_3\text{CN}/\text{C}_3\text{H}_6^+$ encounter complex. The product distribution $m/z = 45$ versus $m/z = 58$ is in line with previous experiments^{4a,9}) which demonstrated that electron impact ionization of cyclopropane or dissociative ionization of tetrahydrofuran (loss of CH_2O) give rise to a mixture of ca. 80% $\text{CH}_3\text{CHCH}_2^+$ (i.e. the propene radical cation) and ca. 20% ionized cyclopropane, the latter having a one-electron C–C bond¹⁰). In these studies^{4a,9}) it was also demonstrated that H^+ transfer originates from $\text{CH}_3\text{CH}=\text{CH}_2^+$, while ionized cyclopropane in its ring-opened distonic form reacts by CH_2^+ transfer.

Scheme 3



In order to obtain indications on the structure(s) of the $\text{CH}_3\text{CN}/\text{CH}_2^+$ species, ab initio MO calculations on several conceivable candidates were performed. These include the

traditional adduct **4**, the CH or CC insertion product **5** and two species, **6** and **7**, which are the results of hydrogen migrations from the CH_2 unit of **4** to either the nitrile carbon (**6**) or nitrogen atom (**7**)¹¹). From the energy data, given in Table 1, it follows that the most stable isomer corresponds to **4**, i.e. addition of CH_2^+ to the electron lone pair of the nitrogen atom. While **6** is only marginally higher in energy (14.7 kcal/mol), the insertion product, ionized propanenitrile **5**, as well as **7** are significantly less stable at this level of theory. More importantly, by using these data and known thermochemical data the heat of reaction for CH_2^+ transfer from **2** to CH_3CN is negative only for the productions of **4** and **6**. In contrast, the generation of the CH/CC insertion product **5** is calculated to be 38.5 kcal/mol endothermic, in quite good agreement with experimental data (35.6 kcal/mol)¹²). In view of the fact that under ICR conditions endothermic processes have extremely small rate coefficients, if they occur at all, the theoretical results already rule out the direct formation of **5** and **7** as products of the CH_2^+ transfer from **2** to CH_3CN . Even in the reaction of $\text{CH}_2\text{OCH}_2^+$ (**3**) with CH_3CN ^{4d}), which is 26 kcal/mol more exothermic than the reaction of CH_3CN with **2**, formation of the CH/CC insertion product **5** can be ruled out on thermochemical grounds as the overall process would still be endothermic.

Table 1. Calculated energies of some $\text{C}_3\text{H}_5\text{N}^+$ isomers and heats of reaction, ΔH_r^0 , for CH_2^+ transfer from **2** to CH_3CN

Species	$\langle S^2 \rangle$	Total energy 3-21G//3-21G [Hartree]	ZPVE [kcal/mol]	E_{rel} [kcal/mol]	ΔH_r^0 [kcal/mol]
$\text{CH}_3\text{CNCH}_2^+$ (4)	0.76	-169.71844	47.3	0	-37.8
$\text{CH}_3\text{CH}_2\text{CN}^+$ (5)	0.79	-169.59690	49.2	76.3	+38.5
$\text{CH}_3\text{C(H)NCH}^+$ (6)	0.77	-169.69507	47.1	14.7	-23.1
$\text{CH}_3\text{CN(H)CH}^+$ (7)	0.75	-169.57292	46.9	91.3	+53.5

Table 2. CID mass spectra of $\text{CX}_3\text{CN}/\text{CY}_2^+$ ions ($X, Y = \text{H}, \text{D}$) with pulsed Ar in the presence of CX_3CN ^a)

m/z	$\text{CH}_3\text{CN}/\text{CH}_2^+$ (4)	$\text{CD}_3\text{CN}/\text{CH}_2^+$ (4a)	$\text{CH}_3\text{CN}/\text{CHD}^+$ (4b)	$\text{CH}_3\text{CN}/\text{CD}_2^+$ (4c)
58		7.9 (63.7)		
57		4.7 (24.8)		10.9 (46.1)
56			9.4 (40.5)	
55	4.5 (54.3)			2.5 (6.9)
54	4.5 (21.8)		5.1 (15.0)	
46		38.6		
45		78.8 (11.5)		
43				36.8 (24.0)
42	91 (23.9)		85.5 (44.5)	49.8 (23.0)

^a) Intensities are expressed in Σ ions = 100%. The figures given in parentheses refer to a CID experiment in which both the collision gas Argon and the reaction partner CX_3CN are introduced through pulsed valves (see text).

In view of the fact that we did not succeed in localizing a transition structure for the isomerization **4** \rightarrow **6** it remains open, for the time being, whether the internal energy gained in the CH_2^+ transfer according to Scheme 2 is sufficient to

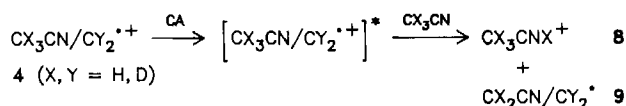
permit this reaction to occur. We suggest that the initially formed species very likely corresponds to the previously suggested radical ion **4**, i.e. $\text{CH}_3\text{CN}-\text{CH}_2^+$. However, the dissociation reactions of $\text{CH}_3\text{CN}-\text{CH}_2^+$ provide experimental evidence that the isomerization **4** \rightarrow **6** takes place in the course of collisional excitation of mass-selected $\text{CH}_3\text{CN}/\text{CH}_2^+$ ions and their isotopomers.

Collisional activation of the "isolated" species $\text{CX}_3\text{CN}/\text{CY}_2^+$ (X, Y = H, D) with pulsed argon (pulse duration 1 μs ; reaction time 0.5 s) gives rise to the products shown in Table 2. Two products are observed which correspond to the losses of H^*/D^* and CY^* (Y = H, D), respectively, the latter being the more favoured process.

Let us first discuss the formation of the species $m/z = 42$, 43 which are due to formal loss of CY^* from the precursor complexes **4**–**4c** involving the CY_2 moiety, added to acetonitrile in its reaction with **2** and its isotopomers. The sheer presence of signals at $m/z = 46$ in the spectrum of **4a** and at $m/z = 42$ in the spectrum of **4c** requires that, in addition to a simple isomerization/dissociation mechanism, decomposition of $\text{CX}_3\text{CN}/\text{CY}_2^+$ (X, Y = H, D) must involve a *bimolecular* component in which the neutral CX_3CN species are involved [Note, that the experiment is performed at a constant background pressure (ca. 3×10^{-9} mbar) of CX_3CN . For a variant of the experiment, see below]. Out of the many conceivable possibilities⁷⁾, on energetic grounds the most likely one corresponds to a reaction sequence, depicted in Scheme 4. Collisional activation (CA) of **4** (and its isotopomers) generates translationally excited species **4*** which serve as *protonating species* of neutral CX_3CN . From the labeling data, given in Table 2, it follows that only the methyl group of **4*** serves as proton source in Scheme 4. According to the MO calculations (3-21G), proton transfer involving the CY_2 unit of **4*** would be less favoured by 38 kcal/mol¹³⁾.

Further support for the operation of a bimolecular proton-transfer reaction in the collision-induced dissociation of $\text{CX}_3\text{CN}/\text{CY}_2^+$ is provided by the following experiment: If the reaction time is increased, the ratio ($m/z = 46$)/($m/z = 45$) for $\text{CD}_3\text{CN}/\text{CH}_2^+$ increases and that of ($m/z = 43$)/($m/z = 42$) for $\text{CH}_3\text{CN}/\text{CD}_2^+$ decreases continuously. This is exactly what one would expect if a bimolecular process, as depicted in Scheme 4, participates in the reactions of $\text{CX}_3\text{-CN}/\text{CY}_2^+$ ¹⁴⁾.

Scheme 4



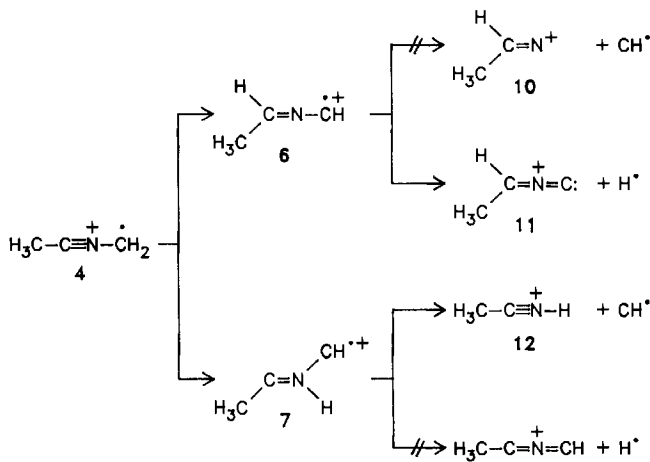
The proposal that collision-induced dissociation of $\text{CX}_3\text{-CN}/\text{CY}_2^+$ proceeds, to some extent, according to Scheme 4, is further substantiated by an experiment in which the neutral reaction partner CX_3CN is not present at a constant, relatively high background pressure but is rather pulsed-in, as is the actual collision gas Ar. The data given in paren-

theses of Table 2 are extracted from experiments performed with an excitation pulse of $t = 5 \mu\text{s}$ and a reaction time of 2 s. The data reveal that under this condition loss of H^*/D^* and of CY^* are the only processes operative¹⁵⁾. The absence of a signal at $m/z = 46$ in the spectrum of $\text{CD}_3\text{CN}/\text{CH}_2^+$ (**4a**) clearly indicates that in spite of the relatively long reaction time of the collision experiment, the bimolecular transfer of D^+ does not take place. However, in the analogous experiment with $\text{CH}_3\text{CN}/\text{CD}_2^+$ the signal due to the bimolecular process (i.e. $m/z = 42$) is still present, and high resolution of the signal confirms its elemental composition ($\text{C}_2\text{H}_4\text{N}^+$). As will be shown below, these results are not contradictory but rather point to the decisive role *kinetic isotope* effects play in both the bimolecular proton (deuterium) transfer as well as in the unimolecular isomerization/dissociation path involving the CY_2 unit of $\text{CX}_3\text{CN}/\text{CY}_2^+$: For the $\text{CD}_3\text{CN}/\text{CH}_2^+$ precursor the bimolecular D^+ transfer is suppressed, while for the $\text{CH}_3\text{CN}/\text{CD}_2^+$ isotopomer it is the isomerization/dissociation path which is subject to a large isotope effect thus permitting the bimolecular variant.

With regard to the mechanism of the unimolecular component of the dissociation of $\text{CX}_3\text{CN}/\text{CY}_2^+$, which forms the major portion of the two competing reaction channels, the study of $\text{CH}_3\text{CN}/\text{CHD}^+$ (**4b**) is quite revealing. The data in Table 2 demonstrate that **4b** undergoes exclusive loss of CD^* ($m/z = 42$); a signal at $m/z = 43$ which would correspond to the elimination of CH^* is not present in the spectrum. Obviously, dissociation of **4** is preceded by a hydrogen migration which is subject to a very large kinetic isotope effect resulting in the complete suppression of deuterium migration.

Conceivable intermediates in the loss of CH^* from **4** are **6** and **7** (Scheme 5)¹⁶⁾. Although **6** is substantially more stable than **7**, the dissociation step **7** \rightarrow **12** + CH^* is, according to 3-21G, 111 kcal/mol more favoured than process **6** \rightarrow **10** + CH^* . This is mainly due to the fact that the proton affinity (PA) of the nitrile carbon atom of RCN is significantly smaller than the PA of the nitrogen atom of RCN. It should be recalled, that the lower homologue of **10** (i.e. H_2CN^+) exists only as an energy-rich triplet cation¹⁷⁾.

Scheme 5



With regard to the collision-induced hydrogen (deuterium) loss from CX_3CN/CY_2^+ ($X, Y = H, D$) the interpretation of the experimental data (Table 2) is straightforward. The CX_3 group does not serve as a source for the generation of hydrogen (deuterium); rather, it is the methylene unit from which the hydrogen (deuterium) atom originates [specific losses of H^{\bullet} from CD_3CN/CH_2^+ (**4a**) and of D^{\bullet} from CH_3CN/CD_2^+ (**4c**)]. Obviously, no scrambling precedes the dissociation step. However, the observation that CH_3CN/CHD^+ (**4b**) undergoes exclusive elimination of D^{\bullet} (no signal at $m/z = 55$ is present in the spectrum) makes it mandatory to postulate the operation of a migration preceding the actual dissociation step. As in the case of CY^{\bullet} loss, the hydrogen rearrangement, in comparison with migration of a deuterium, is so fast that the latter is completely suppressed with the consequence that CH_3CN/CHD^+ (**4b**) undergoes specific elimination of D^{\bullet} . Conceivable intermediates are, again, species **6** and **7** (Scheme 5). However, in contrast to the formation of CH^{\bullet} , the ab initio MO studies suggest that for the hydrogen atom loss the reaction involving **6** is, in its exit channel, by 31 kcal/mol more favourable than process $7 \rightarrow 13^{16}$.

B) Reactions of $CH_2XCH_2^+$ ($X = O, CH_2$) with Alkynes

The reaction of $CH_3C\equiv CH$ with ionized cyclopropane gives rise to many products, among which the $C_4H_6^+$ ion is a prominent one. This species corresponds to a CH_2^+ transfer to propyne. There are many structures conceivable for the $C_4H_6^+$ product, and the most likely ones having negative reaction enthalpies for the process $CH_3C\equiv CH + C_3H_6^+ \rightarrow C_4H_6^+ + C_2H_4$ are given in Table 3.

Table 3. Reaction enthalpies, ΔH_f^0 , for the process $CH_3C\equiv CH + C_3H_6^+ \rightarrow C_4H_6^+ + C_2H_4$ ^{a)}

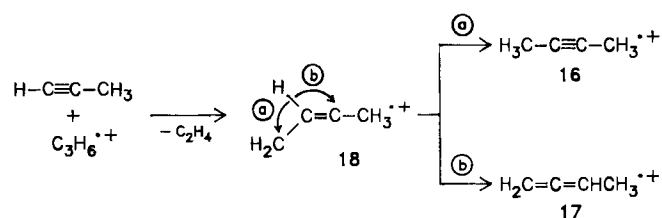
	ΔH_f^0 [kcal/mol]
$CH_2=CH-CH=CH_2^+$ (14)	-40.4
$HC\equiv C-CH_2CH_3^+$ (15)	-2.7
$CH_3C\equiv CCH_3^+$ (16)	-21.9
$CH_2=C=CHCH_3^+$ (17)	-17.7

^{a)} Data were taken from ref. ^{9c,12}.

Many experiments⁷⁾ were performed aimed at structurally characterizing the $C_4H_6^+$ ion formed in CH_2^+ transfer to $CH_3C\equiv CH$. Low-energy CID experiments of the "isolated" $C_4H_6^+$ species (or its $C_4H_4D_2^+$ isotopomer formed by CD_2^+ transfer from $C_3D_6^+$) proved unsuccessful. The observed collision-induced losses of H^{\bullet} and CH_3^{\bullet} are not structure-indicative, and the observation that $CH_{3-x}D_x$ ($x = 0-2$) are formed in a nearly statistical manner are in line with previous results¹⁸⁾ pointing to rapid interconversion of several $C_4H_6^+$ isomers. However, a structural characterization was achieved by subjecting the "isolated" $C_4H_6^+$ ion to ion-molecule reactions with several hydrocarbons. Before describing these results, it is worth recalling that Gross and Russell¹⁹⁾ have already demonstrated that a distinction is possible. For example, in the ion-molecule reaction of

$CH_2=CH-CH=CH_2^+$ (**14**) with 1-butene three products are formed corresponding to $m/z = 95$ ($C_7H_{11}^+$; loss of CH_3^{\bullet} from the encounter complex), $m/z = 82$ ($C_6H_{10}^+$; loss of C_2H_4), and $m/z = 81$ ($C_6H_9^+$; loss of $C_2H_5^{\bullet}$). In contrast, $HC\equiv CCH_2CH_3^+$ (**15**) gives rise to the formation of $m/z = 95$ and $m/z = 81$ (no $m/z = 82$). In the reactions of either $CH_3C\equiv CCH_3^+$ (**16**) or $CH_2=C=CHCH_3^+$ (**17**) with 1-butene one observes only one signal at $m/z = 95$. Similarly, the reactions of $C_4H_6^+$ with 1-pentene can be used to structurally distinguish several $C_4H_6^+$ isomers. The following experiment was performed: $C_4H_6^+$ was generated from $CH_3C\equiv CH$ and ionized cyclopropane at a constant background pressure of propyne (7×10^{-9} mbar). After a reaction time of 2 s the $C_4H_6^+$ ion was "isolated", excitation was brought about by an RF pulse ($t = 10 \mu s$), and the $C_4H_6^{+*}$ species reacted with pulsed-in 1-butene (collision time 100 ms). Under these conditions, the only product ion observed corresponds to $C_7H_{11}^+$ ($m/z = 95$). Thus, CH_2^+ transfer to $CH_3C\equiv CH$ does neither result in the formation of ionized butadiene (**14**) nor of 1-butyne (**15**). Rather, the data implies that the resulting ions correspond to the radical cations of 2-butyne (**16**) and 1,2-butadiene (**17**), respectively, which are presumably formed in competition from a common intermediate. The same conclusion was arrived at by using 1-pentene instead of 1-butene. A further distinction between **16** and **17** could not be achieved. A possible mechanism for the CH_2^+ transfer to $CH_3C\equiv CH$ is suggested in Scheme 6. We note that the formation of **16** formally corresponds to an insertion of CH_2^+ into a $C(sp)-H$ bond; of course, the actual path involves a multistep methylene-cation addition/hydrogen migration process. Although the product stabilities (see Table 3) would favour path \textcircled{a} over path \textcircled{b} , in the absence of reliable information on the barriers of the two competing processes no quantitative data on the product distribution **16** versus **17** can be given.

Scheme 6

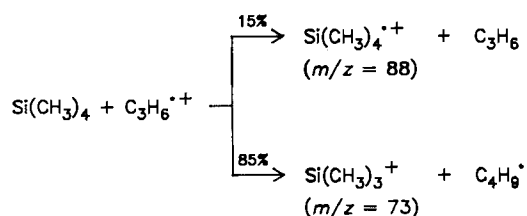


In view of the promising results obtained for the $CH_3C\equiv CH/CH_2^+$ system and the fact that the potential surface of the lower homologue, i.e. $C_3H_4^+$ is quite well understood²⁰⁾, we have subjected $HC\equiv CH$ to a CH_2^+ transfer experiment. The fact that the reaction of C_2H_2 with $C_3H_6^+$, to initially generate $CH_2-C(H)=CH^+$ (the lower homologue of **18**), is endothermic by 6.3 kcal/mol has led us not to use $CH_2CH_2CH_2^+$ (**2**) but rather to employ the distonic ion $CH_2OCH_2^+$ (**3**) as a CH_2^+ transfer reagent; for the reaction of the latter with C_2H_2 to generate $CH_2-CH=CH^+$ we estimate $\Delta H_f = -19.4$ kcal/mol. However, no signal due to $C_3H_4^+$ could be detected; instead an intense

signal at $m/z = 39$ is observed which, in line with theoretical predictions²⁰, points to a rapid loss of H^+ from the intermediate $C_3H_4^+$.

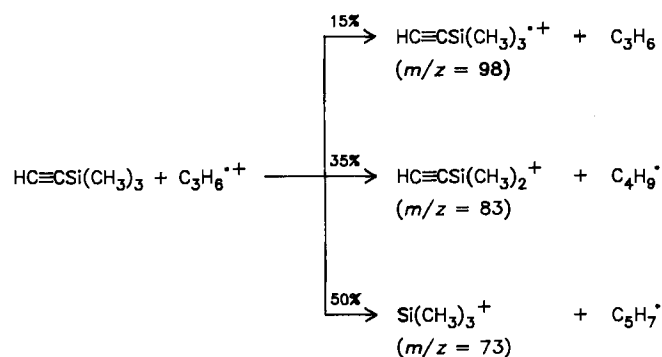
Experiments were also conducted with silyl-substituted species, not the least hoping that both thermochemical (relatively weak $Si-X$ bond) and kinetic factors [relatively high lying MO's of $\sigma(Si-X)$ bonds] might favour a direct insertion of CH_2^+ into an $Si-X$ bond. Of course, we were aware of the fact that electron transfer from the neutral Si compound to the distonic ions might efficiently compete with CH_2^+ transfer. In fact, in the reactions of $Si(CH_3)_4$ with $CH_2XCH_2^+$ ($X = CH_2, O$) the only products are due to transfer of negatively charged species from $Si(CH_3)_4$ to the distonic ions. Scheme 7 summarizes the results for the reaction with $C_3H_6^+$ (2). Noteworthy is the facile transfer of a methyl anion. Double-resonance experiments confirm that $m/z = 73$ is not formed by loss of CH_3 from $m/z = 88$. Products due to a CH_2^+ transfer are absent in the spectra.

Scheme 7



A similar result is obtained for the reaction of $C_3H_6^+$ with trimethylsilylacetylene. In addition to electron transfer we obtain signals for the transfer of either a methyl and an acetylide anion (Scheme 8). Again, no signals were detected for a possible CH_2^+ attachment to $HC\equiv CSi(CH_3)_3$.

Scheme 8



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Experimental

FTICR experiments were performed²¹ with a Spectrospin CMS 47X instrument equipped with an external ion source²² of conventional design in which the distonic ions 2 and 3 were generated by dissociative ionization (70 eV electron impact) of appropriate precursors^{2b,d}. After extraction from the source, the ions are transferred through a system of electric potentials and lenses into the analyzer cell, where they are decelerated, trapped, allowed to undergo various ion-molecule reactions, and the reaction products are eventually detected. The ion source, the transfer system and the ICR cell are differentially pumped by three turbomolecular pumps (Balzers TPU 330 for the source and the cell and Balzers TPU 50 in the middle of the transfer system). The pressure in the ion source is monitored by a Balzers PKG 020 Pirani gauge, while the pressure in the analyzer region is measured by an uncalibrated ionization gauge (Balzers IMG 070).

The superconducting magnet (Oxford Instruments) has a maximum field strength of 7.05 Tesla and a 15-cm room-temperature bore. The cylindrical cell has a radius of 3 cm and a length of 6.1 cm. All functions of the instrument are controlled by a 24-bit/768-K Bruker Aspect 3000 computer; for data storage a 160-MByte Winchester disk, an 8-inch floppy disk or a Cipher M-890 streamer-tape are employed. The broadband spectra were recorded with the fast 9-bit ADC as 32-K or 128-K data points and subjected to one zero fill before Fourier transformation. Plotting the spectra was performed with a Nicolet ZETA 8 plotter.

After "isolation" of the ions of interest by using double-resonance ejection pulses²³, the ions are allowed to react for a variable time (typically several ms up to a few s) with the organic bases **B** present at a constant pressure of ca. 10^{-8} mbar. The organic substrates and Argon [used as the collision gas to bring about collision-induced dissociation (CID)²⁴ of the products formed in the reactions of 2 and 3 with **B**] were introduced either through two leak valves or with the help of two pulsed valves²⁵. The kinetic energy of the ions, which is of importance for the course of ion-molecule reactions, was varied by changing the duration of the radiofrequency (RF) excitation pulse, keeping the amplitude of the RF pulse constant. In addition, by employing the pulsed-valve technique and varying the time interval of the collision experiments the kinetic parameter operative in the CID experiments can be controlled.

The labeled compounds were either obtained commercially or synthesized⁷ by using standard laboratory procedures; they were purified by gas chromatography and identified by spectroscopic methods.

The ab initio MO calculations were performed using the GAUSSIAN 82 programme package (CRAY-XMP version)²⁶. Open-shell species were treated in the unrestricted and closed-shell molecules in the restricted Hartree-Fock formalism²⁷. The geometries were fully optimized with the split-valence 3-21G basis set²⁸ using analytical gradient techniques. Stationary points were characterized by evaluating the force constant matrix. Zero-point vibrational energies (ZPVE) have been calculated from the 3-21G harmonic normal frequencies without scaling. In order to estimate the degree of spin contamination, the $\langle S^2 \rangle$ values were calculated. In view of the quite limited basis set used and the fact that no electron correlation effects are included, the MO results have, at best, qualitative character — numerical accuracy is not aspired to. As has been shown, the MO results are nevertheless quite helpful in the interpretation and understanding of the experiments.

CAS Registry Numbers

2: 60836-41-1 / 3: 74427-28-4 / MeCN: 75-05-8 / MeC≡CH: 74-99-7 / Me₄Si: 75-76-3 / TMSC≡CH: 1066-54-2 / D₂: 7782-39-0

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