human platelet thromboxane synthetase inhibiting activity in vitro.[32] In summary, the biological profile displayed by **2** is consistent with that of a TxA_2 agonist. The agonist profile of **2**, in contrast to the mixed activities exhibited by the carbon analogues of TxA_2, indicates that the bicyclic acetal structure of TxA_2, the assignment of which was based on indirect evidence,[1] plays a key role in the activity of the natural material. Furthermore, the reduced activity exhibited by **28** suggests that position of the acetal oxygens is important for activity. A detailed description of these results will be the subject of a forthcoming publication.

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Discrimination of $C_3H_3^+$ Structures on the Basis of Chemical Reactivity

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The ion $C_3H_3^+$ is one of the more ubiquitous ions observed in the mass spectral patterns of organic compounds. It is also the most abundant ion species observed in fuel-rich acetylene and benzene flames,[1] where it has been suggested to be an important precursor in the mechanism leading to soot formation.

There is ample evidence from studies of metastable ion fragmentation processes and measurements of kinetic energy release in such fragmentations in alkanes,[2] allyl halides,[3] the 1-halo-1-propynes,[4] and the propargyl halides[4,5] that $C_3H_3^+$ exists in two structures. According to theoretical calculations,[6] the cyclic $C_3H_3^+$ structure (with a heat of formation of 11.1 eV) is the most stable isomer. The propargyl ion, CH_2CCH^+, with a heat of formation approximately 1 eV higher, is the next most stable form.[4] These have been identified as the most probable structures for the $C_3H_3^+$ ions observed in the fragmentation processes.[2–5]

Although a few rate constants and reaction mechanisms for $C_3H_3^+$ have been reported,[7] only Munson[8] in a 1967 study of the ionic reactions in *n*-butane remarked on the "peculiar" pressure dependence of the abundance of $C_3H_3^+$, which he suggested might be caused by the presence of two different $C_3H_3^+$ species. All other kinetic measurements have tacitly assumed that the reactant $C_3H_3^+$ species had a unique structure.

Here we report results on the kinetics of the reactions of $C_3H_3^+$ species which show that both isomers retain distinct identities as long as $\sim 10^{-3}$ s (the collision interval in the ion cyclotron resonance spectrometer) and that their chemistry is quite different. The formation of $C_3H_3^+$ in a number of precursor compounds through dissociative charge-transfer processes is shown to result in strongly energy-dependent variations in the relative abundances of the two isomers. Reactions of both isomers with a number of organic compounds, including acetylene and benzene, were observed.

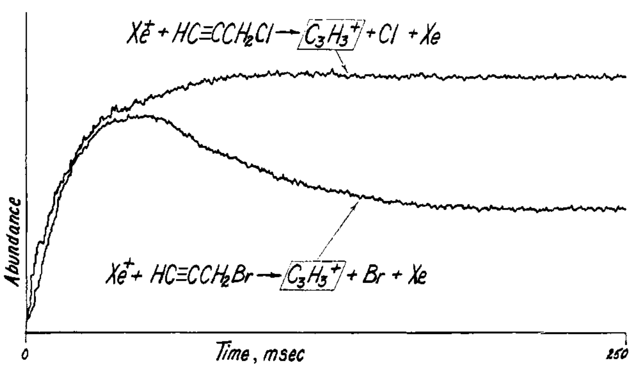

Figure 1. The abundance of $C_3H_3^+$ ions in $Xe–CH{\equiv}CCH_2Br$ (20:1) and $Xe–CH{\equiv}CCH_2Cl$ (20:1) mixtures as a function of time. Nominal electron energy, 60 eV; total pressure, 10^{-5} torr.

A pulsed ion cyclotron resonance spectrometer (ICR) was utilized in this work.[9] A description of the approach used to distinguish between isomeric ions through their kinetic differences has been given.[10,11]

Figure 1 shows the abundance of $C_3H_3^+$ as a function of time in two different systems ($Xe–CH{\equiv}CCH_2Br$ and $Xe–CH{\equiv}CCH_2Cl$ mixtures), chosen as an illustration of a system in which two distinct populations of $C_3H_3^+$ are evident, and a system in which all $C_3H_3^+$ ions apparently have the same (unreactive) structure. In the $CH{\equiv}CCH_2Br$ system, a fraction of the $C_3H_3^+$ ions react rapidly with the parent molecule

$$\mathit{C_3H_3}^+ + \mathrm{C_3H_3X} \rightarrow \mathrm{C_6H_6}^+ + \mathrm{X} \qquad (1)$$

(where X is Br for the $CH{\equiv}CCH_2Br$ reactant, and $\mathit{C_3H_3}^+$ is the more reactive isomer, to be distinguished from ($C_3H_3^+$), the other isomer). An upper limit of 10^{-12} cm^3/molecule·s can be ascribed to the rate constant for reaction of ($C_3H_3^+$) with $CH{\equiv}CCH_2Br$, while $\mathit{C_3H_3}^+$ reacts at essentially every collison.

The relative abundances of the $\mathit{C_3H_3}^+$ and ($C_3H_3^+$) populations are given in Table I for various binary systems where $C_3H_3^+$ is predominantly produced by the dissociative charge-transfer process[12]

$$M^+ + C_3H_3X \rightarrow C_3H_3^+ + X + M \qquad (2)$$

(where X is a halogen atom, and M represents a rare gas atom or a diatomic or triatomic molecule). The rate constants for the overall charge transfer from M^+ to C_3H_3X are also given in Table I. In every case measured here, the charge transfer occurs at every collison; the variations in the rate constants listed in Table I follow with remarkable fidelity the changes predicted from the changes in the reduced mass of the various reacting pairs. The photoelectron spectra of $CH{\equiv}CCH_2Cl$ and $CH{\equiv}CCH_2Br$[13] consist of well-defined bands with a gap between ~ 11.5 and ~ 14.5 eV; yet charge-transfer processes which fall within this energy gap

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(12) The relative abundances of $\mathit{C_3H_3}^+$ and ($C_3H_3^+$) listed in Table I were derived from experimental tracings of ion abundance as a function of time, like those pictured in Figure 1. The abundance of ($C_3H_3^+$) is taken as equal to the observed abundance of unreactive ions (i.e., the flat portion of the curve seen at long times), while the abundance of $\mathit{C_3H_3}^+$ is estimated by taking the difference between the observed maximum in the curve and the level portion. It is recognized that this procedure necessarily underestimates the relative importance of the $\mathit{C_3H_3}^+$ population because a fraction (estimated from the rate of increase of the corresponding product ions to be about 10–30%) will have reacted with the parent molecule by the time the maximum is reached.

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Table I. Relative Abundances of CH_2CCH^+ and c-$C_3H_3^+$ Ions Formed in the Process $M^+ + CH{\equiv}CCH_2X$ (X = Br, Cl) → $C_3H_3^+ + M + X$. Rate Constants of the Charge-Transfer Reactions

		C_3H_3Br[d]			C_3H_3Cl[e]		
M	IP(M), eV	$[C_3H_3^+/(\mathrm{C_3H_3}^+)]$[c]	k_{CT},[a] cm³/molecule·s × 10^{10}	Z_{calcd},[b] cm³/molecule·s × 10^{10}	$C_3H_3^+/(\mathrm{C_3H_3}^+)$	k_{CT},[a] cm³/molecule·s × 10^{10}	Z_{calcd},[b] cm³/molecule·s × 10^{10}
COS	11.2	<0.05	n.d.		<0.05	n.d.	
O_2	12.07	0.1	19.1	17.8	<0.05	15.7	19.0
Xe	12.13	0.75	11.5	11.3	<0.05	12.8	13.0
N_2O	12.9	0.3	15.8	15.3	<0.05	14.9	17.1
CO_2	13.8	0.6	15.7	14.3	<0.05	13.4	17.1
CO	14.0	0.5	20.5	18.7	0.5	16.1	19.9
Kr	14.0	0.25	14.0	12.7	0.4	10.2	14.3
N_2	15.6	0.1	25.3	18.7	0.14	19.1	19.9
Ar	15.76	0.12	18.4	16.3	0.18	n.d.	

[a] Rate constant for the total charge transfer $M^+ + C_3H_3X$, including dissociative and nondissociative channels. [b] Rate constant for collision of ($M^+ + C_3H_3X$) calculated using the ADO formulation (Bowers, M. T.; Su, T. "Theory of Ion-Polar Molecule Collision" In "Interactions Between Ions and Molecules"; Ausloos, P., Ed.; Plenum: New York, 1974 and references cited therein) taking values of 7.6 and 8.8 × 10^{-24} cm³ for the polarizabilities of C_3H_3Cl and C_3H_3Br, respectively, and values of 1.68 and 1.52 × 10^{-18} esu as the respective dipole moments. [c] See text. $C_3H_3^+ \equiv CH_2CCH^+$; $(\mathrm{C_3H_3}^+) \equiv$ c-$\mathrm{C_3H_3}^+$. See also ref 12. [d] Calculated appearance potentials:[4] c-$C_3H_3^+$, 10.06 eV; CH_2CCH^+, 11.18 eV. [e] Calculated appearance potentials:[4] c-$C_3H_3^+$, 10.67 eV; CH_2CCH^+, 11.79 eV.

are highly efficient, demonstrating that restrictions due to Franck–Condon factors can be significantly modified in thermal energy charge-transfer reactions.

Pronounced variations of the ratio $C_3H_3^+/(\mathrm{C_3H_3}^+)$ are observed with changes in both charge donor and charge acceptor (Table I). For instance, a substantial proportion of the $\mathrm{C_3H_3}^+$ has the reactive $C_3H_3^+$ structure when formed through charge transfer from Xe^+ to $CH{\equiv}CCH_2Br$, while for the $CH{\equiv}CCH_2Cl$ precursor, charge donors of considerably higher energy are required before a significant fraction of the $\mathrm{C_3H_3}^+$ ions are observed to have the $C_3H_3^+$ structure. In fact, a significant population of $C_3H_3^+$ is observed in $CH{\equiv}CCH_2Cl$ only when the charge donor has an ionization potential as high as 14 eV (CO, Kr). Furthermore, for both $CH{\equiv}CCH_2Br$ and $CH{\equiv}CCH_2Cl$ presursors, the proportion of $\mathrm{C_3H_3}^+$ ions observed in the reactive $C_3H_3^+$ structure diminishes as the exothermicity of the charge transfer from M^+ increases. Apparently, the highly internally excited $C_3H_3^+$ ions formed in the initial fragmentation have the ability to dissociate or rearrange to $(\mathrm{C_3H_3}^+)$ prior to collision; $C_3H_2^+$ ions are observed. In this regard, it should be noted that a fivefold change in the ratio $M/CH{\equiv}CCH_2X$ from 10 to 50 has no influence on the observed ratio of the two $\mathrm{C_3H_3}^+$ isomers, indicating that these unimolecular processes occur at times shorter than 10^{-3} s.

Charge transfer from Ar^+ and Kr^+ to $CH_2{=}C{=}CH_2$, $CH_3C{\equiv}CH$, $CH_3CH_2C{\equiv}CH$, and $CH{\equiv}CCH_2CH_2C{\equiv}CH$ results in the formation of $\mathrm{C_3H_3}^+$ ions of both structures, with more of the reactive isomer formed in the Ar^+-sensitized experiments than in the Kr^+-sensitized systems. In contrast, no $C_3H_3^+$ species were formed when benzene or $CH_3C{\equiv}CC{\equiv}CCH_3$ were ionized by charge transfer from Ar^+.

The variations in the relative abundances of $C_3H_3^+$ and $(\mathrm{C_3H_3}^+)$ with the recombination energy of the charge donor M^+ show an apparently higher onset energy for the formation of $C_3H_3^+$, suggesting CH_2CCH^+ as the identity of this species. The $(\mathrm{C_3H_3}^+)$ ion would then be identified as having the lower energy cyclopropenium structure. Corroborative evidence for these assignments is found in the fact that all of the compounds shown to give significant abundances of $C_3H_3^+$ are molecules from which a simple C–C or C–H bond cleavage could lead to the formation of CH_2CCH^+. Furthermore, Baer et al.[14] have reported that for $CH{\equiv}CCH_2CH_2C{\equiv}CH$, the ratio of the fragment ions $C_3H_3^+/C_4H_4^+$ shows a much greater increase at energies above 16 eV than does the same ratio observed in benzene or $CH_3C{\equiv}CC{\equiv}CCH_3$. Apparently, the latter two C_6H_6 isomers decay via a common path to c-$C_3H_3^+$ over a wide energy range, while at energies above 16 eV, $CH{\equiv}CCH_2CH_2C{\equiv}CH$ undergoes a direct scission of the central carbon bond to form CH_2CCH^+.

The reactions of CH_2CCH^+ (i.e., $C_3H_3^+$ were investigated by generating these ions in Xe–$CH{\equiv}CCH_2Br$ mixtures in the presence of various reactant molecules. The following reactions with acetylene were observed:

$$CH_2CCH^+ + C_2H_2 \rightarrow C_5H_5^+ \quad k_{(3)} = 10\text{–}15 \times 10^{-10}\ \mathrm{cm^3/molecule{\cdot}s} \tag{3a}$$

$$CH_2CCH^+ + C_2H_2 \rightarrow C_5H_3^+ + H_2 \tag{3b}$$

Both the $C_5H_5^+$ and $C_5H_3^+$ ions formed in reaction 3 exhibit reactive and unreactive populations, indicating that they are each formed with two distinct structures. The reactive $C_5H_5^+$ and $C_5H_3^+$ species yield $C_7H_5^+$ upon reaction with acetylene:

$$C_5H_5^+ + C_2H_2 \rightarrow C_7H_5^+ + H_2 \tag{4}$$

$$C_5H_3^+ + C_2H_2 \rightarrow C_7H_5^+ \tag{5}$$

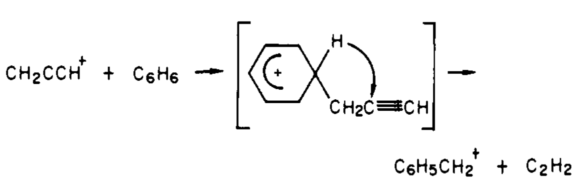
The major hydrocarbon ions observed in acetylene flames are $C_3H_3^+$, $C_5H_3^+$, and $C_7H_5^+$.[1]

The propargyl ion reacts with benzene as follows:

$$CH_2CCH^+ + C_6H_6 \rightarrow C_9H_7^+ + H_2 \tag{6a}$$

$$CH_2CCH^+ + C_6H_6 \rightarrow C_7H_7^+ + C_2H_2 \tag{6b}$$

It was determined through the observation of the characteristic reaction of $C_6H_5CH_2^+$ with toluene[15] that at least 80% of the $C_7H_7^+$ ions formed in reaction 6b were formed with the benzyl structure. In view of this, the mechanism of reaction 6b can be envisioned as follows:



(7)

In a tandem Dempster ion cyclotron resonance study of the ion–molecule reactions in benzene,[16] $C_3H_3^+$ ions of unspecified structure were observed to react to form $C_9H_7^+$ and $C_7H_7^+$.

The CH_2CCH^+ ion undergoes efficient reactions with other hydrocarbon compounds. For example, a hydride transfer is observed for alkane reactant molecules having three or more carbon atoms:

$$CH_2CCH^+ + RH \rightarrow C_3H_4 + R^+ \tag{8}$$

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The ion undergoes condensation reactions, as well as hydride transfer, with alkyl benzenes and condensation reactions (with and without loss of H_2 from the product ion) with olefins.

Even though cyclopropenium ions [i.e., $(C_3H_3^+)$] are unreactive with the propargyl halides, acetylene, and benzene, these ions are observed to react with a variety of compounds, although usually at a much lower rate than the corresponding reactions of CH_2CCH^+. For instance, c-$C_3H_3^+$ reacts with unsaturated molecules having four or more carbon atoms by condensation. This ion also reacts with aldehydes by hydride transfer and with amines through several mechanisms including hydride transfer and condensation [$k \sim (1-10) \times 10^{-10}$ cm^3/molecule·s]. The cyclic ions do not react with linear or branched alkanes (C_4–C_{10}), even though reactions which are exothermic by as much as 10 or 15 kcal/mol can be written for these systems.

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Synthesis and X-ray Crystal Structure of a Soluble Divalent Organosamarium Complex

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For many years, the organometallic chemistry of the lanthanide elements has centered primarily on the 3+ oxidation state.[2] During the past few years, we have investigated the low valent chemistry of the lanthanide elements in an effort to develop a more extensive chemistry for these metals than is found for their trivalent complexes,[3-8] and recently, interest in this area has increased considerably.[9-11] As part of our research program, we have used the metal vaporization technique[12-18] to examine the reactivity of the zero-valent lanthanides with neutral unsaturated hydrocarbons. These reactions have provided a variety of new classes of organolanthanide complexes,[3,5,6,8] including some which display catalytic activity.[5,6] We report here the utility of this low valent approach to lanthanide chemistry in providing access to soluble divalent organosamarium complexes. These complexes are especially significant in light of recent interest in applying divalent lanthanide chemistry to organic synthesis[19,20] and catalytic reactions involving the Ln(III)/Ln(II) couple.[7,9] Sm(II) is the most reactive of the readily accessible divalent lanthanides [Sm(III) + e → Sm(II):–1.50 V[21]], but the only previously synthesized Sm(II) organometallics, $(C_5H_5)_2Sm$[22] and $(CH_3C_5H_4)_2Sm$,[23] are insoluble and hence of limited utility.

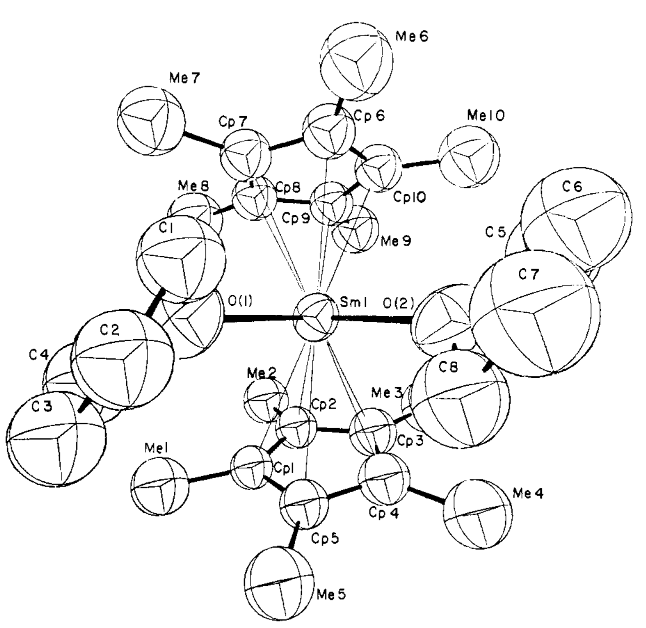

Figure 1. ORTEP plot of the molecular structure of $(C_5Me_5)_2Sm(THF)_2$.

Vaporization of samarium metal into a mixture of pentamethylcyclopentadiene in hexane in a rotary metal vaporization reactor[24] cooled by a petroleum ether slush bath kept at ca. –120 °C generates a yellow, then green, and finally black solution over a period of 40 min. Filtration of the green-black reaction mixture at room temperature in an inert atmosphere glove box separates a solid, which, after washing with hexane and toluene, can be extracted with tetrahydrofuran (THF) to form a purple-brown solution. Removal of THF from this solution gives a product which contains Sm(II) and hydride ligands based on complete elemental analysis, magnetic susceptibility, and deuteriolytic decomposition which forms HD and D_2 in a 1.9:1 ratio.[25] Attempts to obtain crystals of this reactive hydride from THF at low temperature result in decomposition and/or ligand redistribution reactions

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(25) Complete elemental analysis (Bernhardt) of this product is consistent with the formula $C_5Me_5SmH(THF)_2$, the product expected from simple oxidative addition of C_5Me_5H to samarium. Anal. Calcd for $SmC_{18}H_{32}O_2$: Sm, 34.98; C, 50.30; H, 7.26; O, 7.44. Found: Sm, 35.09; C, 50.28; H, 7.26; O, 7.37 (by difference). However, the magnetic susceptibility of the sample, $\chi_M^{296} = 3400 \times 10^{-6}$ was less than that expected for a pure Sm(II) complex [4800×10^{-6} ($\mu = 3.4$) to 5400×10^{-6} ($\mu = 3.6$)] and deuteriolysis gave less than the quantitative amount of gas expected (0.85 mol/mol of Sm). These data could arise from a divalent hydride (which does not quantitatively hydrolyze and which has a low magnetic susceptibility at room temperature) or from a product containing a 2:1 mixture of a divalent hydride plus a trivalent hydride such as $(C_5Me_5)_2SmH$. If the latter product is present, its decomposition to I has precedent in organoytterbium chemistry.[7]

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