10 Gas phase organic ion–molecule reaction chemistry

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1 Introduction

Mass spectrometry continues to be an exceptionally versatile approach for studying molecular structure, reactivity and thermochemistry. Over the past 20 years, it has played an important role in unraveling the mechanisms of many gas phase organic reactions. Although the majority of organic chemistry is completed in the condensed phase, gas phase studies yield very useful information about the intrinsic reactivity of systems (*i.e.*, in the absence of solvation and ion pairing effects). The gas phase results allow chemists to clearly differentiate between solvation effects and factors related to the structures of the reaction partners. In this way, the gas phase studies complement those from the condensed phase and allow chemists to study the intimate details of reaction mechanisms.

In addition to traditional physical organic data such as product distributions and rate constants, ion–molecule reactions can yield physical properties such as gas phase acidities, basicities, and bond energies. Ion–molecule reactions are also a promising tool for solving difficult analytical problems because the reactions are often highly selective and extremely fast. Instruments for the study of ion–molecule reactions include flowing afterglows (FA), selected ion flow tubes (SIFT), Fourier transform ion cyclotron resonance mass spectrometers (FT-ICR or FT-MS), quadrupole ion trap mass spectrometers (QITMS), high-pressure mass spectrometers (HPMS), and ion beam systems. The basic operating principles and limitations of each of the experimental methods are beyond the scope of this review.

The present paper reviews studies of gas phase organic ion–molecule reactions that were published in 1999. In developing this review it was necessary to set arbitrary boundaries on the chemistry that would be included. First, the focus is on bimolecular reactions. Unimolecular reactions initiated by ionization or collisional activation are ubiquitous and provide a foundation for chemical analysis by mass spectrometry; however, they are outside the scope of the review. Second, organometallic reactions have been excluded. In recent years, gas phase organometallic chemistry has become an extensive field with a strong focus on the bonding properties of bare or partially coordinated metals. It truly represents a distinct field and deserves a separate review. Third, the reactions of large

biomolecules have not been included because the great majority of the studies have been limited to simple proton transfer processes rather than functional group transformations. Finally, the present review is generally limited to experimental studies; however, theoretical studies that are intimately associated with experimental work have been included.

In recent years, numerous reviews have been presented on topics related to gas phase organic ion chemistry including the following: organic ions,[1] electrophilic reactions with aromatic substrates,[2,3] nucleophilic displacement reactions,[4] radical anions,[5] molecular cluster reactions,[6] fullerene carbon clusters,[7,8] sulfur-[9] and silicon-[10,11] containing ions, gas phase ion–atom reactions,[12] atmospheric ion chemistry,[13] interstellar and circumstellar chemistry,[14] the analytical applications of ion–molecule reactions,[15–17] multiply charged ions,[18,19] anhydrous protein ions,[20] and three body ion–molecule reactions.[21] These reviews provide a foundation for the material presented here.

2 Reactions of carbocations and related cations

Carbocations still play a central role in gas phase organic chemistry. During 1999, a number of aspects of carbocation reactivity were probed. Studies of electrophilic aromatic substitution continued, ring-forming reactions involving acyl cations were presented, and factors that affect carbocation stability were investigated. In addition, several studies have focused on the reactions of radical cations.

A. Carbocation reactions

The reactions of simple carbocations with aromatic systems were the subject of three studies. Tsuji *et al.*[22] investigated the reactivity of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ with five singly substituted benzenes, PhX [X = NH_2, $NHCH_3$, $N(CH_3)_2$, NO_2, and CN] in a quadrupole ion trap. Under the reaction conditions (10^{-4} torr), the dominant processes were proton transfer and charge transfer; however, moderate yields of addition products were observed for each of the aromatic systems with $C_3H_5^+$. In addition, $C_3H_5^+$ gave a 10% yield of O^- abstraction from nitrobenzene to give the nitrosobenzene cation and a radical [eqn. (1)].

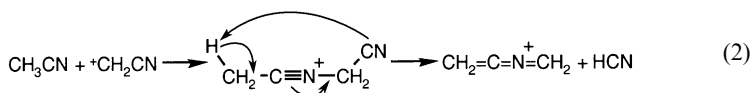$$C_6H_5NO_2 + C_3H_5^+ \longrightarrow C_6H_5NO^{+\bullet} + C_3H_5O^{\bullet} \qquad (1)$$

The reactions of polycyclic aromatic hydrocarbons (PAH's) with the ions derived from the ionization of perfluorotributylamine were studied by Mosi *et al.*[23] in a quadrupole ion trap. The products resulting from these reactions generally consisted of $[M + R]^+$ adducts and $[M + R - nHF]^+$ addition/elimination products. The relative abundance of these products depends on the structure and ionization potential of the PAH. The same group studied the reactions of PAH's with cations derived from the ionization of dimethyl ether ($^+CH_2OCH_3$, $(CH_3)_2OH^+$, and $(CH_3)_3O^+$).[24]

The methoxymethyl cation, $^+CH_2OCH_3$, undergoes a well-known addition/elimination process[25] with the loss of CH_3OH and presumably the formation of a benzylic-like carbocation. The other ions, $(CH_3)_2OH^+$ and $(CH_3)_3O^+$, gave no reactions with PAH's other than proton transfer. Satterfield and Brodbelt[26] found that in reactions of the methoxymethyl cation with pilocarpine, a biologically important compound that contains both an imidazole and a butyrolactone ring, methylation occurs on the imidazole ring rather than the lactone ring. This is in accord with the higher methyl cation affinity of the imidazole group.

Electrophilic aromatic substitution was also investigated for borazine ($B_3N_3H_6$), an inorganic analog of benzene. Chiavarino et al.[27] used the radiolytic method as well as an FT-ICR to study the reactions of borazine and its methyl-substituted derivatives with electrophiles. When treated with reagents such as $(CH_3)_2F^+$, $(CH_3)_2CH^+$ and $(CH_3)_3C^+$, borazine gave electrophilic substitution products (i.e., methyl, isopropyl and tert-butyl borazine, respectively) in the radiolytic experiments. The authors presented a mechanism involving alkylation of the nitrogen followed by proton transfer to a neutral base in the reaction mixture. Surprisingly, methyl substitution reduces the reactivity of the borazine derivatives whereas it increases the reactivity of benzene derivatives (i.e., toluene is more reactive than benzene in electrophilic aromatic substitution).

The details of the reaction of the cyanomethyl cation with acetonitrile were studied by Oldham[28] in a quadrupole mass spectrometer using isotopically labeled species. The work confirmed an earlier mechanism from Moneti et al.[29] and showed that after the formation of an addition product, concerted HCN expulsion leads to the $CH_2=C=N=CH_2^+$ cation [eqn. (2)].

$$CH_3CN + {}^+CH_2CN \longrightarrow \underset{CH_2-C\equiv N^+-CH_2}{\overset{H \qquad CN}{}} \longrightarrow CH_2=C=\overset{+}{N}=CH_2 + HCN \qquad (2)$$

Oldham and Svatos[30] have used this resulting cation in reactions with long-chain alkenes and found that the products give useful information concerning the position of the double bond in the alkene.

Using a pentaquadrupole, triple-stage mass spectrometer, Eberlin and co-workers[31] have discovered a distinct selectivity in the reactions of acyl cations with cyclic acetals. In earlier work with five- and six-membered ring acetals,[32,33] they had observed transacylation reactions that involved the loss of $CH_2=O$ (Scheme 1). In the present work, it was found that seven-membered ring acetals, 1,3-dioxepane and 1,3-dioxep-5-ene, allow for a second pathway that involves a ring contraction. Reaction with an ^{18}O labeled acetyl cation initially leads to an addition product which ring opens to an acyclic ester containing an oxygen-stabilized methyl cation at the end of the chain (Scheme 1). When five- and six-membered ring acetals are used, the carbonyl carbon of the ester acts as a nucleophile and displaces $CH_2=O$ to give five- and six-membered ring products, respectively. However when seven-membered ring acetals are used, either ester oxygen can act as a nucleophile and a mixture of five- and seven-membered ring products is formed.
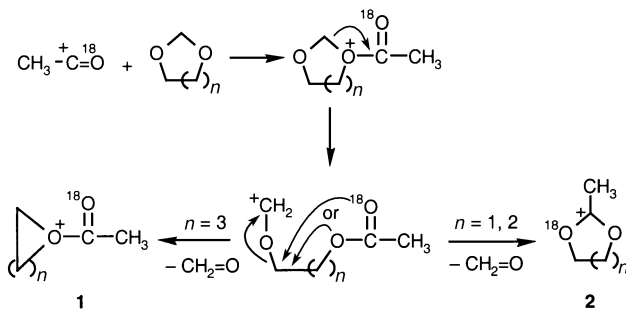
Scheme 1

Collision-induced dissociation (CID) of the products reveals the mixture because fragmentation of **2** should give a roughly 1:1 mixture of labeled and unlabeled acetyl cations, but **1** is expected to yield only labeled acetyl cations. The preference for the ring contraction pathway in the present system was rationalized on the basis of the entropic advantage of ring closure to a five-membered ring rather than a seven-membered ring.

Sharifi and Einhorn[34] have investigated the reactions of acyl cations with diene-bearing epoxides and have identified products that suggest Diels–Alder reactions. The authors propose that the initially formed cycloaddition product undergoes a ring opening followed by a series of rearrangements and finally the expulsion of a carbonyl species to give pyrylium product ions [eqn. (3)].

$$(3)$$
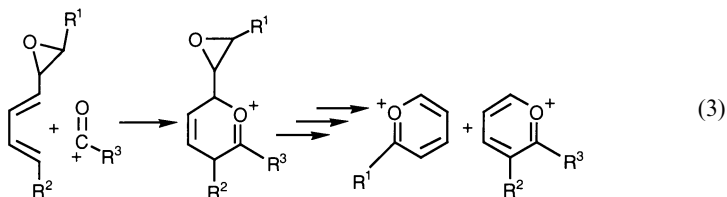
Bortolini *et al.*[35] have reported the ion–molecule reactions of carbon suboxide C_3O_2 with several ions including $(C_2H_2N)^+$, $(C_3H_4N)^+$, H_3O^+, $C_3O_2^{+\bullet}$, $CH_3CH=CH_2^{+\bullet}$, and $N_2^{+\bullet}$. The reaction products are consistent with addition at the central carbon of C_3O_2 followed by a single or double CO loss, often resulting in net carbon atom transfer to the cation.

Abboud *et al.*[36,37] have taken advantage of dissociative proton addition (DPA) reactions in an FT-ICR to investigate the stability of bridgehead carbocations. In this approach, a carbocation is formed as the result of the protonation and subsequent heterolytic cleavage of a $C–XH^+$ or $C–OH_2^+$ bond in an alkyl halide or alcohol, respectively [eqn. (4)].

$$R-Z + AH^+ \xrightarrow[Z\,=\,OH,\,Cl,\,Br]{DPA} R^+ + HZ + A \qquad (4)$$
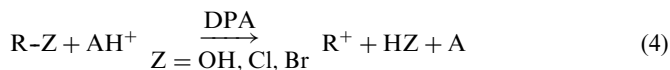
In these systems, the acidity of the proton donor directly relates to the exothermicity of the cleavage process and therefore one can characterize the stability of the carbocation by determining the DPA threshold (*i.e.*, the weakest acid that leads to cleavage). Sixteen different bridgehead systems were investigated including adamantyl, norbornyl, and cubyl systems, and the data lead to a very good correlation between the gas phase carbocation stability and the condensed phase solvolysis rate of the corresponding halide (log k). Therefore it appears that the solvolysis rates are governed by the intrinsic stability of the carbocation and solvent does not preferentially stabilize the transition states of any of the systems in the study.
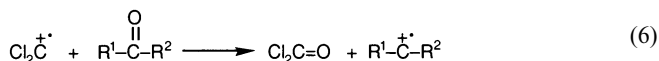
Morton and co-workers[38] have used a labeled substrate to study the gas phase rearrangements of 3-fluoropropyl cations derived from the ionization of 3-fluoropropyl phenyl ethers. In their system (EBFlow reactor), it is possible to collect the neutral products of the reactions and identify them spectroscopically (NMR). Products associated with both 1,2- and 1,3-hydrogen shifts are observed. Although the 1,3-shift is thermodynamically favored (formation of an α-fluorocarbocation), it is disfavored kinetically relative to a 1,2 shift by a factor of about 10:1.

B. Radical cation reactions

Nixdorf and Grützmacher[39] have investigated the reactions of the methylamine radical cation with a group of ethene derivatives bearing one or two halogens (Cl or Br). The reactions proceed by nitrogen addition to the double bond to give a distonic radical cation intermediate which breaks down by expulsion of a halogen radical yielding a protonated enamine. In addition, 1,1-dihaloethenes give good yields of $CH_2NH_2^+$, an ion formed by hydrogen atom transfer to the ethene. Computational work indicates that the hydrogen atom transfer occurs in the initial addition complex. An example involving 1,1-dichloroethene is shown in eqn. (5).

$$(5)$$

1,4 hydrogen shift/elimination
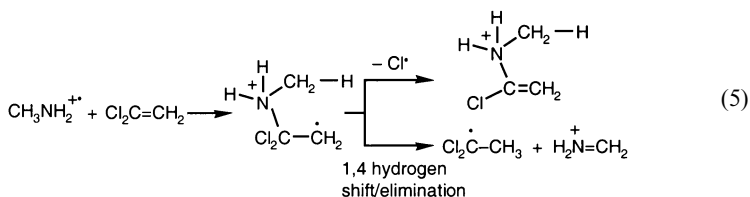
Nelson, Tichy, and Kenttämaa[40] have used an FT-ICR to study the reactions of the radical cation of dichlorocarbene with several organic substrates. The cation is a strong electrophile and reacts in most cases by an atom abstraction process with or without charge transfer. For example, reactions with alkyl halides (R–X) lead to the transfer of a halogen to the carbene and depending on the ionization potentials of the products, CCl_2X^+ or R^+ is produced. Interestingly, the reaction of the dichlorocarbene radical cation with some carbonyl species gives an oxygen atom abstraction process leading to phosgene and a new carbene radical cation that may isomerize to a more stable species [eqn. (6)].

$$Cl_2\overset{+\bullet}{C} \; + \; R^1{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R^2 \longrightarrow \; Cl_2C{=}O \; + \; R^1{-}\overset{+\bullet}{C}{-}R^2 \tag{6}$$

Thissen *et al.*[41] have used an FT-ICR to investigate the reactions of the ethene radical cation with ethene and of the ethyne radical cation with ethane. Using isotopic labels, the details of the reaction mechanisms were explored. The ethene–ethene radical cation system can lead to ionized but-2-ene which undergoes extensive isotopic scrambling before dissociation to give products resulting from loss of $CH_3^\bullet$, $H^\bullet$, and $CH_2{=}CH_2$. The ethane–ethyne radical cation reaction can lead to the formation of the ethyl cation or to a crossover to the intermediates and products of the ethene–ethene radical cation system.

3   Nucleophilic substitution and addition

Nucleophilic substitution and addition are two of the most important processes in organic chemistry and have been investigated in great detail in the gas phase. In recent years, there has been much interest in the potential energy surfaces as well as the dynamics of these gas phase reactions. In 1999, several papers addressed the dynamics issues and others focused on substituent effects on the rates and product distributions of substitution reactions. The highly varied chemistry of carbonyl compounds was probed including acyl substitution and reduction reactions. Finally, the nucleophilic chemistry of some highly reactive, unusual ions was investigated.

A. S_N2 reactions

One of the most widely studied reactions in organic chemistry is bimolecular nucleophilic substitution (S_N2) and over the years there have been numerous studies of gas phase S_N2 reactions. In early work, Brauman[42] showed that gas phase S_N2 reactions have double-well potential energy surfaces. In recent years, many studies have focused on the dynamics of gas phase S_N2 reactions and have questioned whether the reactions can be treated by statistical theories. It is believed that for small systems, the complexes are too short-lived to allow for complete energy randomization and therefore statistical behavior. Hase and his co-workers have

made major contributions to our understanding of the dynamics of gas phase S_N2 reactions during the past 10 years[43] and in 1999, they presented a paper on the application of direct dynamics calculations to the reaction of chloride with methyl chloride at high reagent translational energies.[44] A good correlation with the experimentally determined reaction cross section was found in this study. Ervin[45] also presented a theoretical model for orientational effects in the same reaction.

Using an FT-ICR, Craig, Zhong and Brauman[46] have investigated the effect of translational energy on the rates of two S_N2 identity reactions, $Cl^- + ClCH_2CN$ and $Cl^- + m\text{-}FC_6H_4CH_2Cl$. For both reactions, there is a moderate reduction in the rate constant as the kinetic energy of the chloride is increased; however, the reduction is not as dramatic as those seen in simple systems such as $Cl^- + CH_3Br$. Most importantly, the data can be modeled reasonably well using a statistical approach, RRKM theory. This is in sharp contrast to halide + methyl halide systems and suggests that in larger systems such as these, long-lived encounter complexes lead to nearly complete energy randomization; consequently, statistical treatments are valid. Johnson and co-workers[47a] have used spectroscopy to study the nature of the S_N2 potential energy surface for the reaction of chloride with methyl bromide. They formed the initial ion–dipole complex in this reaction and probed its IR spectrum and its photo-conversion to products. The results are consistent with earlier suggestions that there is inefficient coupling between the reaction coordinate and the C–H motions in the CH_3Br fragment (one of the reasons for non-statistical behavior in this system). The spectroscopic data also point to a C_{3v}-symmetric complex where the chloride resides on the backside of the C–Br axis. In another study involving reaction complexes, Lehmann and Illenberger[47b] presented a novel approach to studying gas phase S_N2 reactions. They have used dissociative electron capture to form reactive halide–alkyl halide ion–dipole complexes starting from van der Waals complexes of the halide precursor and the alkyl halide.

Craig and Brauman[48] have used an FT-ICR to study the effect of internal solvation on the rates of S_N2 reactions. Employing alkyl halides with a polar functional group at the end of the alkyl chain (e.g.,–OH,–Cl, or–CN), they found dramatic rate increases that depend on the location of the functional group relative to the reaction center, but the effect is not directly related to the number of bonds separating the functional group from the reaction center, so a through-space rather than a through-bond interaction is implicated. For example, the cyano group provides the greatest stabilization when it is at an α- or γ-carbon, but is less effective at a β-carbon. Overall, the data suggest that the substituents stabilize the transition states by internal hydrogen bonding or by charge–dipole interactions, both of which are geometry dependent.

Bowie and co-workers[49,50] have studied the intramolecular S_N2 reactions of the 4,5-epoxypentoxide and 5,6-epoxyhexoxide anions. In the former case, the process could lead to a five-membered or a six-membered ring product depending on the point of attack [eqn. (7)].

$$(7)$$

observed   not observed
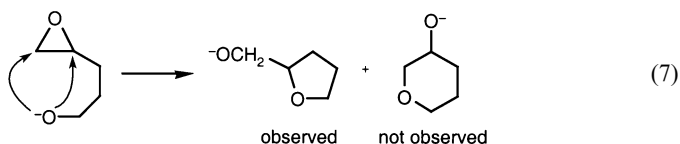
Collision-induced dissociation (CID) of 4,5-epoxypentoxide leads to products that are identical to those from tetrahydrofuran-2-ylmethoxide indicating that cyclization leads exclusively to the five-membered ring product. *Ab initio* calculations indicate that the two cyclizations should have similar enthalpic barriers; therefore, formation of the smaller ring is likely favored by entropic factors. A similar preference for forming the smaller ring (six-membered *vs.* seven-membered) is observed for the 5,6-epoxyhexoxide anion.

Gronert and co-workers[51,52] presented two studies that investigated the competition between substitution and elimination in gas phase reactions. In general, it has been difficult to distinguish between gas phase S_N2 and E2 reactions because with an alkyl halide, both pathways lead to the same ionic product, a halide ion. To overcome this limitation, these workers have used an electrospray source to generate dianions where one ionic site is reactive and the other is inert. The inert ionic site serves as an ionic "handle" for identifying the products. The approach is outlined in Scheme 2. When treated with ethyl bromide, these dianions can be alkylated (S_N2) or protonated (E2) leading to the formation of a pair of anionic products that identify the reaction mechanism. A series of simple alkyl halides (ethyl, propyl, isopropyl, *sec*-butyl, and *tert*-butyl) were used and the expected reactivity trends were observed with an increase in elimination in going from 1° (mainly S_N2) to 3° (all E2) halides. Related computational work indicates that the second charge of a dianion has little effect on S_N2 potential energy surfaces as long as there is a significant charge separation in the initial dianion (15 Å).[53] In another study involving one of the same dianions, Gronert and Azebu[52] formed ion pair complexes with a tetraalkyl-ammonium cation. During collision-induced dissociation (CID), these complexes fragment to give products that are consistent with S_N2 and E2 reactions within the complex (Scheme 3). Interestingly, the E2 reactions exhibit Hofmann behavior with greater elimination yields for the least substituted alkyl groups.
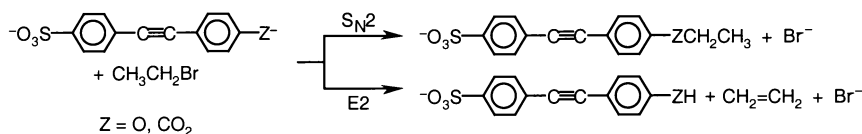

Scheme 2
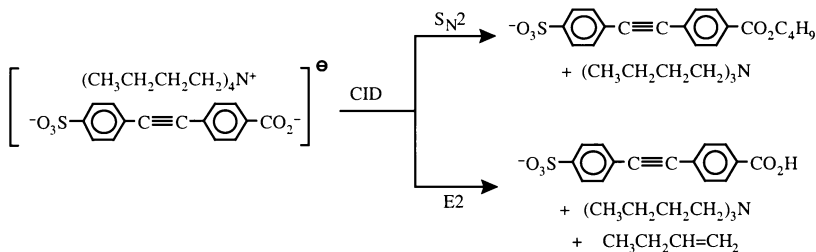
Scheme 3

Finally, Speranza and Filippi[54] have studied the acid catalyzed ring openings of epoxides in the gas phase using the radiolytic method. Starting with a chiral epoxide (styrene oxide), they were able to determine both the regio- and stereochemistry of the reactions in mixtures containing protonated methanol as the reagent. Addition occurs exclusively at the benzylic carbon of the styrene oxide, but they observe a mixture of products resulting from retention or inversion of stereochemistry at the reaction center. Inversion is slightly favored (55–67%) in these gas phase reactions whereas inversion is highly favored in solution. However, unusually high yields of retention products have been observed in previous studies of gas phase, cationic S_N2 processes.[55,56]

B. Addition/elimination and other nucleophilic processes

In 1999, several studies investigated the addition/elimination reactions of nucleophiles with carbonyl species. In a very comprehensive study, Frink and Hadad[57] used a flowing afterglow to examine the product distributions and rate constants of the reactions of formyl and acetyl esters with a range of nucleophiles. Along with proton transfer to give an ester enolate, a number of reaction mechanisms [eqns. (8)–(11)] were identified. They found that although strong bases favor the proton transfer channel, weaker bases give substantial yields of addition/elimination products [eqn. (8)].
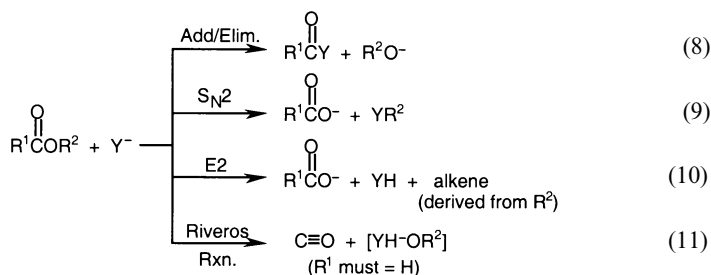
In one study from Brauman's group,[46] the effect of translational excitation on the rates of identity addition/elimination reactions between chloride and substituted benzoyl chlorides was examined. As noted above for S_N2 reactions, large substrates such as these appear to give long-lived encounter complexes, so energy randomization can be nearly complete and statistical models such as RRKM theory can be used to extract thermochemical data from rate constants. In a second study, Zhong and Brauman[58] employed RRKM theory to obtain transition state energies from kinetic data obtained for the reactions of chloride with six benzoyl chloride derivatives [eqn. (12)].

$$Y = H, p\text{-}CH_3, m\text{-}CH_3, m\text{-}OCH_3, m\text{-}F, m\text{-}CF_3 \tag{12}$$
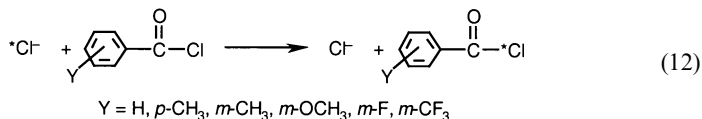
In addition, they determined the complexation energies of these benzoyl chlorides with chloride and consequently had all the data necessary to construct quantitative double-well potential energy surfaces. The results show that electron-withdrawing groups stabilize both the encounter complexes and the addition/elimination transition states, but the effect is greater on the transition states (Hammett plots give slopes of -6 and -10 for the complexation and transition state energies, respectively). As a result, the reaction barriers (relative to the energy of the encounter complex) are reduced when electron-withdrawing groups are present. This is in contrast to the identity S_N2 reactions of chloride with benzyl chloride derivatives[59] where substituents have almost an equal effect on the energies of the transition states and the encounter complexes resulting in a situation where the reaction barriers are nearly the same for all the compounds.

Squires and co-workers[60] have employed pentacoordinate silicon hydride ions, $Bu(RO)SiH_3^-$, as probes of the diastereoselectivity of gas phase ketone reductions in a flowing afterglow. When treated with a ketone or aldehyde, the silicon hydride (R = 3-pentyl) reduces the carbonyl to give an alkoxy siliconate product ion [eqn. (13)].
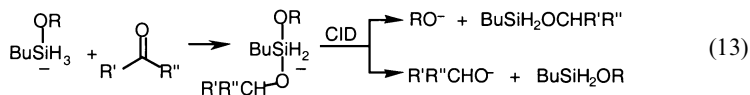
The observed product contains two alkoxy groups (3-pentoxide and the ketone reduction product) and during collision-induced dissociation (CID), either alkoxide can be expelled. The branching ratio is very sensitive to the structure of the alkoxide and therefore provides an analytical tool for determining the diastereoselectivity of the reduction process. For example, in the reduction of 2-methylcyclohexanone,

cis and *trans* 2-methylcyclohexoxide are the expected reduction products and their siliconates will give different branching ratios during CID. By comparison of the observed CID branching ratios with those of authentic samples, the authors were able to determine the yields of each stereoisomer in the reduction process. The approach was applied to five cyclohexanone derivatives and a wide range of stereoselectivities was observed (axial attack yields from 9–99%). Overall, there is a good correlation between the selectivities of the gas phase siliconate reductions and those done in solution under typical conditions (*i.e.*, LiAIH$_4$ in THF).

Bowie and co-workers[61] investigated the Wittig rearrangement of a series of α,α-dialkoxybenzyl anions. This collision-induced, intramolecular reaction can be viewed as an elimination/addition process [eqn. (14)].


$$(14)$$
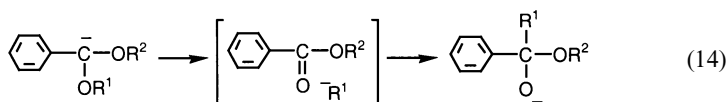
They found that the larger alkyl group migrates preferentially and computational work suggests that the mechanism involves migration of an alkyl anion rather than a radical.

The formation and reactions of unusual anionic species were the subject of several gas phase studies in 1999. Squires and co-workers[62] generated the phenylcarbene radical anion by dissociative electron transfer to phenyldiazirine in a flowing afterglow. This anion is highly reactive as a base, nucleophile, and hydrogen atom abstractor. For example, it removes a sulfur atom from CS$_2$ (presumably to give the thiobenzaldehyde radical anion), a nitrogen from N$_2$O (to give a deprotonated imine), and a hydrogen from CH$_3$SCH$_3$. Moreover, it reacts 40 times faster with methyl chloride (S$_N$2) than the benzyl anion. This work also resulted in a measurement of the phenylcarbene anion's proton affinity (392 kcal mol^{-1}) and its electron binding energy (27.8 kcal mol^{-1}). Treating the same precursor, phenyldiazirine, with hydroxide, Squires and co-workers[63] were able to form the phenylcarbyne anion, C$_6$H$_5$C$^-$. This anion has unusual reactivity with simple substrates and transfers a carbon atom to CO$_2$ to give the phenyl anion. More surprisingly, it abstracts two oxygens from SO$_2$ to give benzoate and atomic sulfur. The acid/base behavior of this ion is not consistent with the computationally predicted proton affinity and the authors believe that within hydrogen bonded complexes (*i.e.*, those formed in the acidity measurements) it is possible for the phenylcarbyne anion to rearrange into a seven-membered ring species [eqn. (15)]. DFT calculations predict that the rearrangement is nearly thermoneutral, but that the product is 10 kcal mol^{-1} more basic than the phenylcarbyne anion. An analogous rearrangement is seen in singlet phenylnitrene, an isoelectronic species.[64]

$$\text{Ph–}C^- \xrightarrow{\ CH_3OH\ } \text{cycloheptatrienyl anion}^- \tag{15}$$
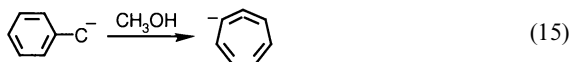
Broadus and Kass[65] have investigated the reactivity of the enolate derived from benzocyclobutenone. Along with determining the thermodynamic properties of the anion (see Section 8.A), they found that it reacts with perfluorobenzene and perfluoropropene mainly as a carbon rather than an oxygen nucleophile [eqn. (16)]. One reason for this preference is that O-alkylation leads to a highly strained, anti-aromatic, benzocyclobutadiene derivative.

$$\text{benzocyclobutenone enolate} + C_6F_6 \text{ or } C_3F_6 \longrightarrow > 95\% \ C\text{-alkylation} \tag{16}$$
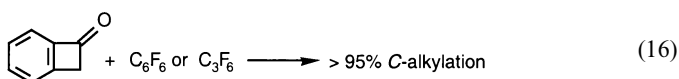
Morris et al.[66] used a flowing afterglow to explore the formation and reactions of CF_3O^-. This ion can be formed as an adduct in the reaction of F^- with $CF_2=O$ or by the reaction of CF_3^- with SO_2. DePuy and co-workers[67] have studied limitations in the hydrogen/deuterium (H/D) exchange reactions of fluorophenyl and difluorophenyl anions ($C_6H_4F^-$, o-$C_6H_3F_2^-$, m-$C_6H_3F_2^-$, p-$C_6H_3F_2^-$) using a SIFT. The $C_6H_4F^-$ anion exchanges all hydrogens for deuterium with D_2O, but the difluorophenyl anions, o-, m-, and p-$C_6H_3F_2^-$, exchange three, two, and one hydrogen, respectively. Reactions with CH_3OD, were also examined and a mechanism was developed that rationalizes the ability/inability of the exchange reagent to move around the aromatic ring system to complete multiple exchanges.

4   Reactions of distonic radical cations and anions

Distonic radical ions contain two possible reaction sites, an ion and a radical, that are localized on different atoms in the molecule. As a result, distonic radical ions can potentially exhibit two different types of reaction chemistries depending on the relative reactivities of the ionic and radical sites. There has been much activity in this area in recent years and much of it has focused on the synthesis and identification of distonic radical cations and anions. This work continued in 1999 and the development of a general route to distonic radical anions was reported.
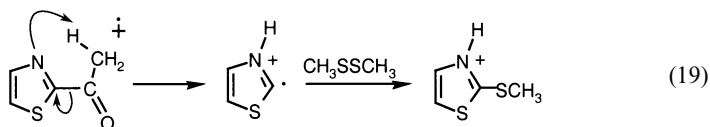
A. Cations

In 1999, Kenttämaa and co-workers[68] introduced another neutral reagent, *tert*-butyl isocyanide, capable of characterizing distonic radical cations. *tert*-Butyl isocyanide displays two distinct types of reactivity involving either the charge or the radical

site in the distonic ion. For example, *tert*-butyl isocyanide can react rapidly with carbocation-containing distonic ions by cyanide ion transfer to give the *tert*-butyl cation [eqn. (17)]. When the charge center is unreactive such as in a pyridinium-substituted phenyl radical, cyano-radical transfer is the exclusive process at a moderate rate [eqn. (18)].

$$\cdot CH_2CH_2OCH_2^+ \xrightarrow{(CH_3)_3CNC} \quad \cdot CH_2CH_2OCH_2CN + (CH_3)_3C^+ \tag{17}$$

$$\tag{18}$$
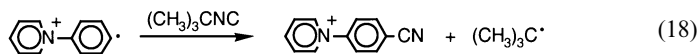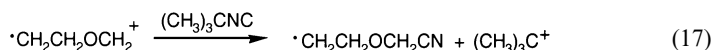
Gerbaux *et al.*[69a] have studied and characterized the 1,2-hydrogen shift isomers of ionized pyridine, thiazole and imidazole. The ion–molecule reactions of these distonic cations with dimethyl disulfide in a hybrid, sector-quadrupole-sector mass spectrometer are distinct from those of their conventional radical cation isomers (*e.g.*, ionized pyridine). Specifically, the distonic cations abstract $CH_3S^\bullet$ radicals whereas the conventional isomers give charge transfer reactions to produce $CH_3SSCH_3^{+\bullet}$. An example involving the thiazol-2-ylidene radical cation (generated by ketene loss from the molecular ion of 2-acetylthiazole) is shown in eqn. (19).

$$\tag{19}$$

The same group[69b] reported a study of a selenium-containing distonic radical cation. The pyridine *N*-selenide radical cation was formed by the reaction of cyanogen *N*-selenide radical cations, $NCCNSe^{+\bullet}$, with neutral pyridine. The resulting radical cation displays some typical distonic ion reactivity, but most commonly undergoes an unusual selenium radical cation transfer to neutral reagents. For example, in the reaction of pyridine *N*-selenide radical cation with CH_3NC, $CH_3NCSe^{+\bullet}$ is formed [eqn. (20)].

$$\tag{20}$$
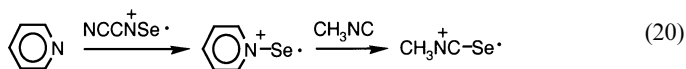
Thoen and Kenttämaa[70] have studied the reactivity of two distonic biradical cations with 15 neutral reagents in an FT-ICR. In these species, a pyridinium ion is attached to either an *ortho* (**3**) or *meta* (**4**) didehydrobenzene.
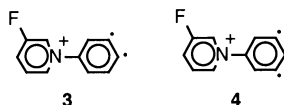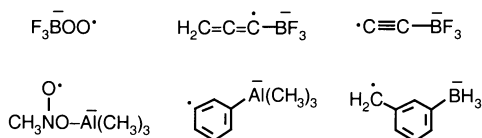

Scheme 4

The *ortho* didehydrobenzene isomer generally undergoes relatively efficient addition reactions with neutral reagents, presumably to give benzene derivatives. In contrast, the *meta* isomer gives slower reactions and, along with addition, radical abstraction reactions are also seen. For example, **3** reacts with benzeneselenol exclusively by addition with an efficiency of 0.34. In contrast, **4** mainly abstracts a hydrogen atom from this reagent with an efficiency of only 0.01. The radical processes seen with **4** are similar to those observed for analogous, distonic phenyl radical cations, but the rate constants are lower. Overall, the *meta* didehydrobenzene distonic biradical cation appears to be less reactive because the greater distance between the radical sites retards the alkyne-like addition reactions observed with the *ortho* isomer, and the stabilizing interaction between the two radical sites retards the radical reactions observed in phenyl radical species.

B. Anions

Squires and co-workers[71] presented an interesting study of the synthesis, structure, and reactivity of distonic radical anions of the "ate"-class. "Ate"-class distonic negative ions are prepared by the addition of neutral Lewis acids, such as BF_3, BH_3, and $AlMe_3$, to radical anions resulting in products with localized anionic sites. The distonic ions can contain either localized σ-type or delocalized π-type radical moieties remote from the relatively inert borate or aluminate charge sites. The free radical reactivity displayed by these ions appears to be independent of the nature of the charge site. Several examples of the "ate" distonic radical anions are shown in Scheme 5.

Scheme 5

These distonic anions undergo addition reactions with open-shelled species like NO and NO_2, but do not abstract $CH_3S^\bullet$ from CH_3SSCH_3, a common, diagnostic reaction for distonic radical ions. The most reactive species, $^\bullet C\equiv C-BF_3^-$, undergoes reactions in which the Lewis acid is displaced [eqn. (21)].

$$^\bullet C\equiv C-BF_3^- \xrightarrow{\ NO_2\ } O_2N-C\equiv C^- + BF_3 \qquad (21)$$
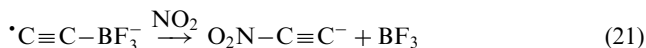
5   Carbon cluster ions

Carbon clusters, including fullerenes, continue to fascinate chemists and have been the subject of numerous mass spectrometry studies. In recent years, several groups have systematically studied the reactions of fullerene and other cluster cations (singly or multiply charged) with a wide range of neutral species. These continued in 1999.

In an important paper, Bohme[8] provided an extensive review of the work that his group has completed on fullerene ions using the SIFT technique. In general, the measured rate coefficients and observed product channels for reactions with a variety of inorganic and organic molecules depend strongly on the charge state of the reactant ion. For fullerene cations, the primary product channels include attachment, dissociative attachment, dissociative attachment with charge separation, single-electron transfer, dissociative single-electron transfer, and two-electron transfer. The higher order chemistry of derivatized C_{60}^{n+} cations is also included in the review and involves cation-transfer reactions, surface derivatization, and ''ball-and-chain'' polymerization.

In 1999, Bohme presented three papers describing new aspects of fullerene cation reactivity.[72–74] In the first,[72] the reactions of $C_{60}^{+\bullet}$, C_{60}^{2+}, and $C_{60}^{3+\bullet}$ with possible chlorination reagents (Cl_2, CCl_4, $CDCl_3$, CH_2Cl_2 and CH_3Cl) were investigated. $C_{60}^{+\bullet}$ and C_{60}^{2+} were unreactive with all of these reagents. The triply charged fullerene, $C_{60}^{3+\bullet}$, does not react with molecular chlorine, but bimolecular chloride transfer and electron transfer reactions were observed with CCl_4, $CDCl_3$, CH_2Cl_2 and CH_3Cl. Chloride transfer is the preferred channel with CCl_4, $CDCl_3$, and CH_2Cl_2 while electron transfer dominates the reaction with CH_3Cl. These results are consistent with trends in chloride affinity and ionization energy. Greater reactivity is often seen in more highly charged fullerenes and the charge separation reactions of the triply charged species are much more exothermic than those of the singly or doubly charged fullerene cations. In a second paper,[73] the reactions of $C_{60}^{+\bullet}$, C_{60}^{2+}, and $C_{60}^{3+\bullet}$ with $CH_2=CHCl$, $CH_2=CCl_2$, $trans$-$CHCl=CHCl$, cis-$CHCl=CHCl$, $CHCl=CCl_2$ and $CCl_2=CCl_2$ were examined. The singly charged fullerene is unreactive and the triply charged fullerene undergoes exclusively fast electron transfer reactions. Intermediate reactivity was observed for C_{60}^{2+} and three product channels were found: electron transfer, adduct formation, and Cl_2 transfer (only for the 1,2-dichloroethene isomers). In addition, polymerization reactions were observed for several of the reagents and a ''ball-and-chain'' mechanism was
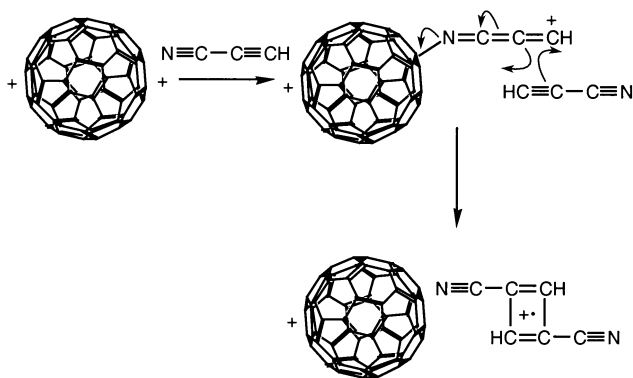
Scheme 6

proposed. The third paper from the Bohme lab[74] describes the identification of the cyanoacetylene dimeric cations produced from two different reactions. The dimer cations, $(HC_3N)_2^{+\bullet}$, were generated in a SIFT either directly by the association of $HC_3N^{+\bullet}$ with HC_3N or indirectly by a sequence of reactions of C_{60}^{2+} with two molecules of HC_3N. The two different isomers of the dimer were identified by collision-induced dissociation. A comparison of computed dissociation energies (DFT) with the observed dissociation pathways and onset energies indicates that the $(HC_3N)_2^{+\bullet}$ formed directly is simply a solvated ion and that the $(HC_3N)_2^{+\bullet}$ produced in the presence of C_{60}^{2+} is a cyclic, dicyanocyclobutadiene cation (Scheme 6). This mechanism provides a general gas-phase reaction route for the cyclization of cyanoacetylenes and could have implications for the dimerization of HC_3N and cyanopolyacetylenes in interstellar/circumstellar environments.

In continuing work on fullerenes, Garvey and co-workers[75] have studied the reaction of C_{60}^{2+} with BCl_3 in a triple-quadrupole mass spectrometer. Along with chloride transfer to give $C_{60}Cl^+$, they observe an unusual C_2 abstraction process that leads to the formation of a series of even-numbered, smaller cluster cations ranging from C_{58}^+ to C_{38}^+. The process does not occur with BF_3 and appears to be related to an initial charge transfer to BCl_3, but no further mechanistic details were obtained in the study.

Grützmacher and co-workers[76] have presented an extensive study of the reactions of smaller carbon clusters, $C_{24}H_x^+$ and $C_{18}H_x^+$ ($x = 0$–12), with benzene. In general, the rate constants increase with decreasing number of H atoms (x) in the reactant cation, but also exhibit an odd/even alternation in reactivity (even-electron $C_{24}H_{2m+1}^+$ cations are generally more reactive than the $C_{24}H_{2m}^{+\bullet}$ odd-electron radical cations). The rate constant of the reaction of benzene with the $C_{24}^{+\bullet}$ carbon cluster ion derived from coronene is three orders of magnitude larger than the same reaction of the monocyclic $C_{24}^{+\bullet}$ carbon cluster ion generated by laser evaporation of graphite. This clearly shows that the $C_{24}^{+\bullet}$ cluster ions from coronene cations do not possess a monocyclic structure and probably retain their polycyclic, aromatic framework.

Ma and co-workers[77] have continued to investigate the reactions of neutral C_{60} with ions and in 1999 described their work on the reactions of the methoxymethyl cation $[CH_3O=CH_2]^+$ and the 1-hydroxyethyl cation $[CH_3CH=OH]^+$ with C_{60}. Adduct ions, $[C_{60}C_2H_5O]^+$, and protonated fullerenes, $[C_{60}H]^+$, were observed as the major products.

6 Reactions of organic ions containing heteroatoms (B, Si, P, S, Cl)

The gas phase chemistry of boron-, silicon-, phosphorus-, sulfur-, and halogen-containing organic ions has been a fruitful area of study because the conditions in mass spectrometers allow for the synthesis of unusual and sometimes highly reactive species in a controlled environment. The following section focuses on systems where the heteroatom carries the charge or plays a pivotal role in stabilizing the ionic site. In 1999, several reactions leading to interesting heterocycles were presented.

Chiavarino and co-workers[78] have investigated the gas-phase reactivity of borazine ($B_3N_3H_6$) and borazine-derived ions using an FT-ICR. The most basic sites in borazine are the nitrogens and its conjugate acid, $B_3N_3H_7^+$, is similar in structure to protonated benzene. The $B_3N_3H_7^+$ ions undergo H/D exchange of up to four hydrogens with CD_3OD suggesting that exchange only occurs on the nitrogens. Borazine is also a hydride donor and reacts with CF_3^+ to give $B_3N_3H_5^+$ ions. In its reactions, borazine is prone to addition/elimination pathways where H_2 often is expelled to give the final product. For example, the major product in the reaction of borazine with fluoride is $B_3N_3H_4F^-$, and methanol gives a significant yield of an addition/elimination product in its reaction with protonated borazine [eqn. (22)].

$$\text{(22)}$$
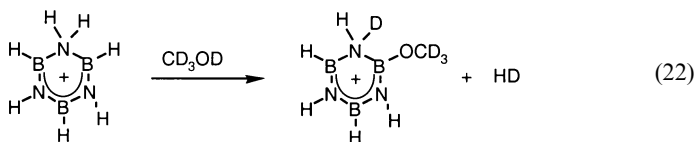
Cooks and co-workers[79] have reported the gas phase synthesis of boron heterocycles from the reactions of cyclic acetals and ketals with borinium $CH_3OB^+OCH_3$ ions. The reactions proceed *via* electrophilic attack of the charged heteroatom on one of the acetal or ketal oxygens followed by consecutive ring-opening and ring-closing processes to give the heterocycle with the loss of a ketone or aldehyde. The reaction is closely related to the Eberlin transacetalization[80] reaction of acylium cations. The process for a borinium cation is shown in eqn. (23).

$$(23)$$
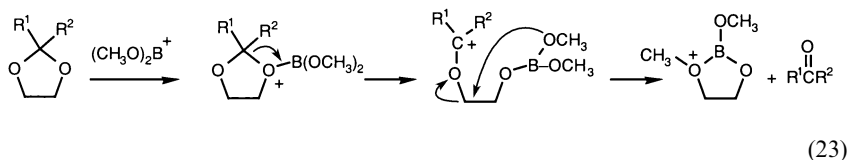
In reactions of the borinium ions with thiazolidine, a similar process is observed and the product ion preferentially retains the sulfur with the loss of a neutral imine. Cooks and co-workers[81] also explored a silicon analogy of the Eberlin transacetalization reaction. When silylium cations (*e.g.*, $^+Si(OCH_3)_3$) react with cyclic acetals or ketals, silicon-containing heterocycles are formed in a reaction process [eqn. (24)] similar to that outlined in eqn. (23) for boron species.

$$(24)$$
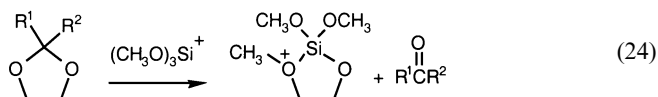
In other studies involving silicon species, Leblanc *et al.*[82] have examined reactions of saturated and unsaturated silyl cations, $(CH_3)_3SiOSi^+(CH_3)_2$ and $CH_2=(CH_3)SiOSi^+(CH_3)_2$, with ketones in an FT-ICR. The product mixtures suggest complex reaction processes and mechanisms were developed on the basis of deuterium labeling studies. The reactions of diethylsilicenium ions, $(C_2H_5)_2SiH^+$, with benzene were studied by Kochina *et al.*[83] using the radiolytic method. Intracluster ion–molecule reactions of various phenylsilane dimer cations were studied by Ishikawa *et al.*[84] Two types of reactions, SiR_3 elimination and SiR_2^+ transfer, were observed within the clusters. Finally, in a series of studies, Antoniotti and co-workers[85,86] have studied the formation of compounds containing both silicon and carbon atoms from the ionization of the following mixtures in an ion trap: $(SiH_4 + C_2H_4)$,[85] $(SiH_4 + C_3H_6)$,[86] $(SiH_4 + C_2H_6)$ and $(SiH_4 + C_2H_2)$.[87] Rate constants for numerous reactions involving silicon cations were reported and the work is supported by DFT computational studies.

Kenttämaa and co-workers[88] have reported the reactions of the dichlorophosphenium ion ($Cl–P^+–Cl$) with cyclic organic ethers in an FT-ICR. Most of the reactions are initiated by $Cl–P^+–Cl$ addition to an oxygen followed by heterolytic C–O bond cleavage. For saturated ethers such as tetrahydrofuran, the most abundant ionic product corresponds to hydroxide abstraction by $Cl–P^+–Cl$. The authors propose a multi-step mechanism that involves heterolytic C–O bond cleavage followed by a 1,2-hydride shift and proton transfer that eventually leads to an allylic cation and $HOPCl_2$. This is shown in eqn. (25).
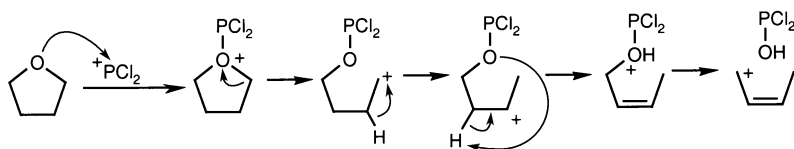
(25)

Adducts formed from most unsaturated ethers do not allow for the necessary hydride shift of this mechanism and proceed through other pathways such as electron transfer, hydride transfer, or O/Cl exchange. As a part of their studies of Eberlin transacetalizations,[80] Cooks and co-workers[79,89] investigated the reactions of two types of phosphorus cations with cyclic acetals. Phosphonium ions readily react with cyclic acetals to give transacetalization products [eqn. (26)]. These reactions are analogous to those presented above for boron and silicon cations.
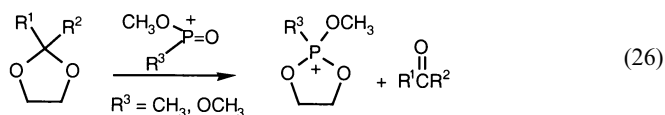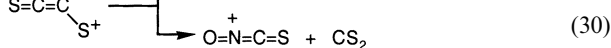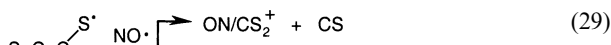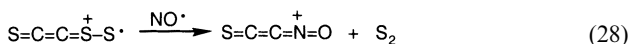
(26)

In the reactions of phosphonium ions with thiazolidine, there is a strong preference for the phosphorus to attack at sulfur leading to a cyclic species with a P–S bond and the loss of an imine. The authors also examined the analogous reactions of phosphenium ions (e.g., $CH_3OP^+OCH_3$) with cyclic acetals, but no trans-acetalization products were observed. Finally, Gal and co-workers[90] used an FT-ICR and an ion trap mass spectrometer to study the ion–molecule reactions observed in the ionization of organophosphorus esters (trimethyl phosphite, triethyl phosphite, dimethyl phosphonate, trimethyl phosphate and 2,2-dichlorovinyl dimethyl phosphate). The phosphonates and phosphates mainly give proton-bound dimers and the phosphites give condensation products of the general formula $[(RO)_3P (RO)_2P]^+$.

Eberlin and co-workers[91] have used pentaquadrupole (QqQqQ) mass spectrometry to explore the reactions of SF_n^+ ($n = 1$–5) ions with benzene, acetonitrile, and pyridine. With benzene, SF^+ reacts by an electrophilic substitution pathway to give benzenesulfenyl fluoride, C_6H_5–$SF^{+\bullet}$, via a Wheland-type intermediate that spontaneously loses an H atom [eqn. (27)].

$$\text{(27)}$$
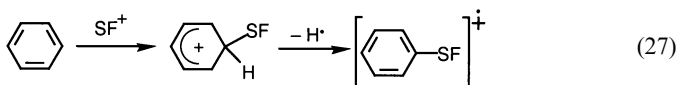
With acetonitrile, $SF_2^{+\bullet}$, SF_3^+, and SF_5^+ give adducts and dimers. It appears that $CH_3-C{=}N-SF_2^{+\bullet}$ (a distonic ion) and $CH_3CN-SF_5^+$ are covalently bound adducts, whereas $[CH_3CN{\cdots}SF_3^+]$ is a loosely bound complex. With pyridine, only SF_3^+ leads to the formation of stable adducts and dimers. Bortolini *et al.*[92] have studied the reactions of the phenylsulfenium cation, $C_6H_5S^+$, with C_2H_2 and CO. In both cases, adducts are formed and *ab initio* calculations as well as CID studies suggest that the bonding occurs on the sulfur. Decker, Adams, and Babcock[93] have explored the reactivity of the radical cations of HSSH and S_2 with a range of simple organic species including alkenes, alcohols, ketones, carboxylic acids, and organic halides. Proton transfer is the most common process for $HSSH^{+\bullet}$, but it does give an unusual product ion with 1,2-difluorobenzene. In this reaction, $C_3H_3FH^{+\bullet}$ is formed in a ring cleavage process with presumably $C_3H_2SSF^\bullet$ as the neutral product. The reactions of $S_2^{+\bullet}$ are much more varied and often multiple product channels are observed including hydride abstraction, charge transfer, and adduct formation. In 1999, three papers used ion–molecule reactions to characterize isomeric ions containing sulfur centers. Flammang and co-workers[94] were able to distinguish between two isomers of $C_2S_3^{+\bullet}$ by reactions with NO. The loss of S_2 [eqn. (28)] *vs.* CS or CS_2 [eqns. (29) and (30)] clearly differentiates between linear *vs.* branched structures for this radical cation.

$$S{=}C{=}C{=}\overset{+}{S}{-}S^\bullet \xrightarrow{\ NO^\bullet\ } S{=}C{=}C{=}\overset{+}{N}{=}O \ + \ S_2 \qquad (28)$$

$$S{=}C{=}C\underset{S^+}{\overset{S^\bullet}{\big\langle}} \xrightarrow{\ NO^\bullet\ } \begin{array}{l} ON/CS_2^+ \ + \ CS \qquad (29) \\[1em] O{=}\overset{+}{N}{=}C{=}S \ + \ CS_2 \qquad (30) \end{array}$$

Flammang's group also used ion–molecule reactions to identify $C_2H_4OS^{+\bullet}$ radical cations that were generated by electron impact on alkyl thioformates[95] and radical cation isomers with the general formula $[CH_3O,C,N,S]^{+\bullet}$ that were generated from various heterocyclic precursors.[96] Kass and co-workers[97] reported the reactivity and thermochemistry of ionic species formed from thiirane derivatives (*i.e.*, thiirane, thiirane *S*-oxide, and thiirane *S,S*-dioxide). When these heterocycles are treated with bases, M−1 ions are formed, but in some cases they undergo ring opening. Evidence for this was found in the ion–molecule reactions as well as the proton affinities of the deprotonation products. For thiirane, a mixture of products is formed [eqn. (31)], but thiirane *S*-oxide gives only ring-opened products [eqn. (32)] and thiirane *S,S*-dioxide does not give any ring-opened products [eqn. (33)].

$$\text{(31)}$$

$$\text{(32)}$$

$$\text{(33)}$$
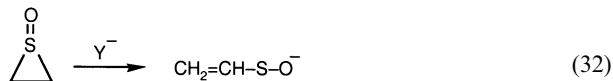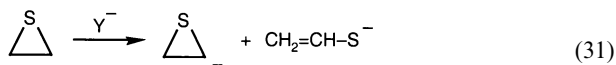
Reactions of the cyclic isomers of these deprotonated heterocycles often lead to ring opening as a result of an exothermic addition process. For example, the reaction of the thiiranyl anion with COS or CS_2 results in sulfur transfer and ring-opening [eqn. (34)]. Proton affinities were determined for the stable heterocyclic anions as well as the ring-opened products.

$$\text{(34)}$$
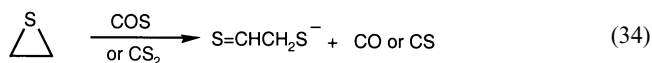
Several studies investigated the formation and reactivity of small chlorine-containing cations. Cacace and co-workers[98] discovered that the powerful chlorinating reagent Cl_3^+ will react with CH_4 by HCl loss and the formation of ions with the formula, $CH_3Cl_2^+$. Two isomers were identified, protonated dichloromethane and CH_3ClCl^+ [eqn. (35)].

$$\text{(35)}$$
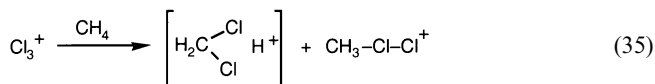
The latter is a potent electrophile and undergoes methyl cation and chlorine cation transfer reactions. de Petris *et al.*[99] found that protonated molecular chlorine will react with both CH_4 and H_2 by insertion mechanisms to give CH_3ClH^+ and $HClH^+$, respectively. As part of a continuing series of papers on the two center, three electron bonds of alkyl halide radical cation dimers, Nichols and Illies[100] studied a group of mixed dimers, $[CH_3X \therefore YCH_3]^{+\bullet}$ (X, Y = F, Cl, Br, I), and reported data on their bond strengths and atomic connectivities. In addition, these authors studied two center, three electron bonds in complexes of methyl halide radical cations and dimethyl sulfide.[101]

7   Reactions of organic compounds with small, inorganic species

The reactions of organic compounds with small, inorganic species play important roles in several fields including atmospheric chemistry, interstellar chemistry, and chemical analysis. Work was completed in each of these areas in 1999.

A. Atmospheric and interstellar chemistry

McEwan and co-workers[102–105] have used a SIFT to study the reactions of many small cations related to atmospheric or interstellar chemistry. In one study,[102] the reactions of $C_mH_n^+$ ions ($m = 1$–6; $n = 0$–6) with atomic and molecular nitrogen were examined. These ions are mainly unreactive with molecular nitrogen, but a range of reactivity was observed with nitrogen atoms. For small cations ($m = 1$–3), nitrogen incorporation into the hydrocarbon cation was observed, but for larger systems ($m = 4$–6), the nitrogen is usually expelled in the form of a neutral molecule (*i.e.*, HCN). Interestingly, C_3^+ reacts very rapidly with nitrogen atoms to give a covalent, nitrile-containing adduct, $CCCN^+$. The reactions of $HCNH^+$, $HC_3N^{+\bullet}$, $H_2C_3N^+$, $H_2O^{+\bullet}$, $N_2^{+\bullet}$, HCO^+, and HCO_2^+ with O atoms have also been studied in a SIFT.[103] Only two of these ions, $HC_3N^{+\bullet}$ and $N_2^{+\bullet}$, react with oxygen atoms and both lead to multiple products. McEwan *et al.*[104] also investigated the reactions of small hydrocarbon ions $C_mH_n^+$ ($m = 1$–6, $n = 0$–9) with H and H_2. Based on the measured three-body association rates, radiative association rate constants were calculated. The results suggest that hydrogen atom addition is a viable mechanism for increasing the saturation level of small hydrocarbon cations in dense interstellar clouds and provides a possible route to benzene in these clouds. Finally, McEwan and co-workers studied two isomers of $C_3H_5^+$, the allyl ($CH_2CHCH_2^+$) and prop-2-enyl ($CH_3CCH_2^+$) cations, and found them to be distinct, non-interconverting species in a flowing afterglow.[105] Reactions with methanol can differentiate between the isomers because while both ions give proton transfer reactions, only the allyl cation can abstract H_2 to give the propyl cation and $CH_2=O$ [eqns. (36) and (37)].

$$CH_2=CH-CH_2^+ \xrightarrow{CH_3OH} CH_3OH_2^+ + C_3H_7^+ + \text{other products} \qquad (36)$$

$$CH_2=C^+-CH_3 \xrightarrow{CH_3OH} CH_3OH_2^+ + \text{adduct} \qquad (37)$$
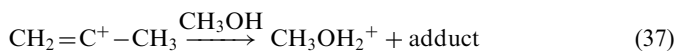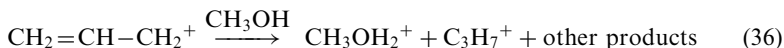
The isomeric ratio of allyl to prop-2-enyl cations formed by protonation of allene or propyne depends on the acidity of the proton donor. Proton transfer to allene from weak acids (*i.e.*, H_3O^+) gives only the prop-2-enyl cation, but stronger acids (*i.e.*, SO_2H^+) give a mixture of allyl and prop-2-enyl cations. The results suggest that the barrier for the rearrangement of the allyl to the prop-2-enyl cation is approximately 26 kcal mol^{-1}.

Temperature dependent rate constants and product branching fractions were reported by Viggiano and co-workers[106] for the reactions of NO^+, $O_2^{+\bullet}$, $O^{+\bullet}$, N^+, $N_2^{+\bullet}$, $N_4^{+\bullet}$, $Kr^{+\bullet}$, $Ar^{+\bullet}$, $Ne^{+\bullet}$, and F^+ with benzene. All of the reactions proceed at the collision rate at all temperatures. Charge transfer and adduct formation are seen for ions with low recombination energies, but dissociative charge transfer is observed for ions with high recombination energies. As a part of this study, dissociation pathways for $C_6H_6^+$ were considered in detail.

Le Page, Keheyan, Snow and Bierbaum[107,108] presented two studies on the reactions of polycyclic aromatic hydrocarbon (PAH) cations with atoms and small molecules of interstellar interest. Using a SIFT, they allowed cations related to pyrene, $C_{16}H_{10}^+$, $C_{16}H_9^+$, and $C_{16}H_{11}^+$, to react with H_2, CO, H_2O and NH_3 molecules as well as H, O, and N atoms.[107] The molecular ion, $C_{16}H_{10}^+$, has no reactivity with the molecules, but does add H, O, and N atoms at moderate to low rates. In contrast, $C_{16}H_9^+$ is much more reactive and forms adducts with CO, H_2O, NH_3, H, O, and N at moderate rates. Protonated pyrene, $C_{16}H_{11}^+$, is generally unreactive with these species and therefore could accumulate in the interstellar medium. Reactions of the naphthalene radical cation and its derivatives ($C_{10}H_n^+$, $n = 6,7,8,9$) with molecules and atoms were also studied.[108] As in the case of pyrene, the radical cation, $C_{10}H_8^+$, is unreactive with H_2, CO, H_2O, and NH_3, but reacts with H, O, and N atoms. Adducts are seen in the reactions of the molecular cation with all of these atoms, but O and N also abstract carbons to produce CO and HCN as neutral products. In this study, a number of pathways were found for the formation of protonated naphthalene (e.g., $C_{10}H_8^+$ + H, $C_{10}H_7^+$ + H_2, and $C_{10}H_6^+$ + H followed by H_2) and it was suggested that it (like other protonated PAH's) may be a terminal ionic species in interstellar syntheses.

Vacher and co-workers[109] have studied clustering equilibria related to Titan's atmosphere. Using a high-pressure mass spectrometer with a radiolytic source, they investigated the thermodynamics of the reactions of acetylene with protonated hydrogen cyanide, $HCNH^+$, and its complexes with N_2, $[HCNH^+N_2]$, and CH_4, $[HCNH^+CH_4]$. Multiple acetylene additions were characterized and it was found that the binding energy to $HCNH^+$ drops monotonically with sequential additions.

In other work with simple cations, Grabowski and co-workers[110,111] studied the reactions of alkenes with $O^{+\bullet}$, OH^+ and $H_2O^{+\bullet}$ in a SIFT. The reactions of $O^{+\bullet}$ with alkenes give high rate constants and extensive fragmentation of the hydrocarbon (<30% of the molecular ion was seen in each case).[110] Other $O^{+\bullet}$ product channels include hydride abstraction ($HO^\bullet$ formation), H_2^- abstraction (H_2O formation), and alkyl anion abstraction ($RO^\bullet$ formation), each yielding a hydrocarbon cation. The authors present a comprehensive mechanistic scheme for the $O^{+\bullet}$ reactions. In the reactions of OH^+ and $H_2O^{+\bullet}$ with ethylene, rates near the collision limit were observed with charge transfer being the dominant process.[111] In addition, $H_2O^{+\bullet}$ gives a significant yield of proton transfer, but surprisingly, no isotope effect was seen in this channel in the reaction of $HOD^{+\bullet}$ with ethylene.

Williams et al.[112] have studied the reactions of a variety of small ions (H_3O^+, D_3^+, $H_2O^{+\bullet}$, D^+, N^+, $D_2^{+\bullet}$, $N_2^{+\bullet}$, $Ar^{+\bullet}$, $Ne^{+\bullet}$, $He_2^{+\bullet}$, and $He^{+\bullet}$) with CCl_4. In most cases, rapid dissociative charge transfer is the dominant mechanism leading to the formation of CCl_3^+, $CCl_2^{+\bullet}$, or CCl^+. In addition, dissociative proton transfer was also observed.

Two studies focused on the reactions of acidic hydrate clusters with organic species. The role of H_2SO_4 in atmospheric ion chemistry was explored by Lovejoy[113] by studying the reactions of $H^+(H_2SO_4)_m(H_2O)_n$ clusters with water, ammonia and organic compounds. In addition, Thomas and Viggiano[114] studied the reactions of $H^+(H_2O)_n$ clusters with dimethyl sulfoxide at temperatures from 198–298 K.

Blanksby and Bowie[14] reviewed recent mass spectrometric studies of interstellar cumulenes and heterocumulenes. Cumulenes are highly unsaturated species containing a series of adjacent double bonds. They have been observed in interstellar clouds and the review describes laboratory studies of possible anionic and cationic pathways to forming these species from simple precursors.

B. Trace analysis

Spanël and Smith continued their systematic SIFT studies of the reactions of simple ions with common organic compounds. In four papers, they analyzed the reactions of H_3O^+, NO^+ and $O_2^{+\bullet}$ with a range of organic species including halohydro-carbons,[115,116] amines,[117] and ketones (NO^+ only).[118] A goal of the work is the development of an analytical method for the detection and quantification of trace gases using the SIFT technique. With H_3O^+, the majority of the reactions are proton transfers to give MH^+ ions, but other reactions, including dissociative proton transfer, occur. For example, halohydrocarbons have a tendency to lose HX (formation of $[M - X]^+$), tertiary amines often lose H_2, and primary amines produce NH_4^+ presumably by proton transfer followed by H_2O substitution to eventually give an alcohol as the neutral product. With NO^+, association is commonly seen with substrates with high ionization energies (*i.e.*, aliphatic halides, ketones) and charge transfer is observed for aromatic halides and amines. For the amines, hydride abstractions (formation of $[M - H]^+$) and dissociative charge transfers (loss of an alkyl group to give $[M - R]^+$) are also observed. With $O_2^{+\bullet}$, high rates are observed and the reactions generally give a mixture of dissociative and non-dissociative charge transfer products. The same group has applied this approach to "real-world" samples including food aromas, urine vapors, and human breath.[119–122]

In 1999, Lindinger and co-workers presented another series of papers detailing their development of proton-transfer reaction mass spectrometry (PTR-MS) as a tool for on-line monitoring of volatile organic compounds (VOCs) at ppt levels. The PTR-MS system[17] is based on rapid proton transfer reactions from H_3O^+ to a substrate within a flow-drift tube. H_3O^+ is chosen as a reactant ion because it does not react with any of the natural components of air and because most of the common VOCs have proton affinities larger than water so fast proton transfers are likely. In the past, it has been used in medical applications, food science, and environmental research. This year, Lindinger presented several studies aimed at detecting trace organics emitted from plants and plant materials including decomposing,[123] damaged,[124] and burning[125] biomass as well as harvested berries.[126] In addition, low levels of benzene were detected in ambient air.[127]
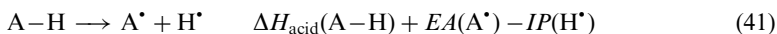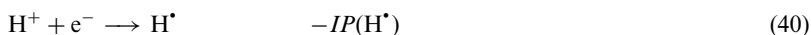
Finally, Reiner and co-workers[128] employed negative ion–molecule reactions to measure the concentrations of acetone, acetic acid, and formic acid in the upper troposphere and lower stratosphere.

## 8 Thermochemical determinations *via* ion–molecule reactions

Mass spectrometry has proven to be an exceptionally powerful tool for determining the fundamental physical properties of organic materials including their acidity, basicity, and bond strengths. The results are often highly accurate and a variety of systems were studied in 1999.

A. Bond energies

In recent years, a number of groups have used a thermochemical cycle involving gas phase acidities and electron affinities to determine homolytic bond strengths.[129] The associated equations are shown [eqns. (38)–(41)].

$$A-H \longrightarrow A^- + H^+ \qquad \Delta H_{acid}(A-H) \qquad (38)$$

$$A^- \longrightarrow A^{\bullet} + e^- \qquad EA(A^{\bullet}) \qquad (39)$$

$$H^+ + e^- \longrightarrow H^{\bullet} \qquad -IP(H^{\bullet}) \qquad (40)$$

$$A-H \longrightarrow A^{\bullet} + H^{\bullet} \qquad \Delta H_{acid}(A-H) + EA(A^{\bullet}) - IP(H^{\bullet}) \qquad (41)$$

The necessary acidities can be derived from a variety of experiments involving mass spectrometry and the electron affinity of the radical can be measured by negative ion photoelectron spectroscopy. Using an FT-ICR, Broadus and Kass[130] have determined a number of the thermodynamic properties of nitrogen deprotonated diaziridine including its proton affinity (390 kcal mol^{-1}) and its electron binding energy (0.50 eV). The ion was prepared in a novel approach involving the gas phase reduction of diazirine with cyclohexadienide [eqn. (42)]. Using the thermodynamic cycle above, this leads to an N–H bond strength of 88 kcal mol^{-1} for the parent diaziridine (c-CN$_2$H$_2$).

$$(42)$$
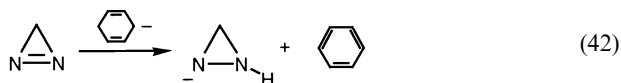
The same authors investigated the proton affinity and electron binding energy of the enolate derived from benzocyclobutenone.[65] Although this ion has potential anti-aromatic character [benzocyclobutadiene fragment in one resonance form, eqn. (43)], its proton affinity (360 kcal mol^{-1}) is not unusually high suggesting that

anti-aromaticity does not have a significant effect on the stability of the ion. Combining the proton affinity with the measured electron binding energy (1.90 eV), they obtain a C_α–H bond strength of 90.5 kcal mol^{-1}.
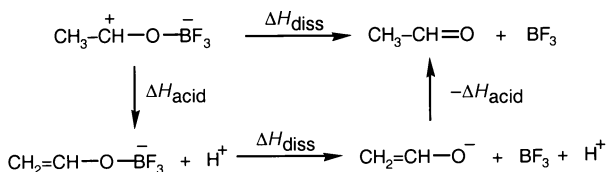
$$\left[\vphantom{\Big|} \text{structure} \longleftrightarrow \text{structure} \right] \tag{43}$$
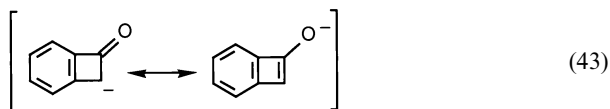
B. Acidities and basicities

All of the studies in 1999 that led to the determination of a gas phase acidity or proton affinity of an organic compound will not be listed here. This information can generally be obtained from the extensive databases maintained by the National Institute of Standards and Technology (NIST, webbook.nist.gov). Below, a few studies are highlighted that have particular relevance to mechanistic or structural physical organic chemistry.

Ren, Cramer, and Squires[131] presented a study of the very low proton affinities of BF$_3$–enolate complexes in the gas phase. Using a thermodynamic cycle (Scheme 7) involving the complexation energy of the enolate with BF$_3$ (experimentally determined), the complexation energy of the parent carbonyl with BF$_3$ (calculated), and the known proton affinity of the bare enolate, they have found that species such as CH$_2$=CR–O–BF$_3^-$ (R = H, CH$_3$, CF$_3$) have proton affinities ranging from 324 to 306 kcal mol^{-1}. Therefore, their conjugate acids (carbonyl–BF$_3$ complexes) can be considered "super-acids" with acidities similar to the strongest gas phase acids (e.g., H$_2$SO$_4$). The authors also found that these carbonyl–BF$_3$ complexes have exceptional hydride affinities (more than 60 kcal mol^{-1} greater than simple aldehydes) and can be classified as "super-electrophiles". McMahon and co-workers[132] completed a study of internal solvation and unconventional hydrogen bonding in alkyl carboxylates. From curvature in van't Hoff plots of proton transfer equilibria with larger carboxylates, they identified two isomeric forms that they believe to be folded (intramolecular hydrogen-bonded) and unfolded. The two forms have fairly similar free energies and co-exist at typical temperatures (300–500 K), but the folded form has a significant enthalpic advantage and entropic disadvantage relative to the unfolded form (−7.3 kcal mol^{-1} and −17.2 eu, respectively, for decanoate). Nibbering and co-workers[133] investigated the anions generated by deprotonation of buta-1,2-diene and but-2-yne. On the basis of their acid/base chemistry as well as their reactions with N$_2$O, neopentyl nitrite and methyl formate, they concluded that the anions were identical. Equilibrium measurements in an FT-ICR lead to gas phase acidities of 376 and 382 kcal mol^{-1} for buta-1,2-diene and but-2-yne, respectively. Zenobi and co-workers[134,135] studied the gas phase basicities of matrix anions that are important in MALDI ion sources. The observed proton affinities of monomers ranged from a high of 347 kcal mol^{-1} for deprotonated

$$CH_3\overset{+}{-}CH-O-\overset{-}{B}F_3 \xrightarrow{\Delta H_{diss}} CH_3-CH=O \ + \ BF_3$$

$\Big\downarrow \Delta H_{acid}$ $\Big\uparrow -\Delta H_{acid}$

$$CH_2=CH-O-\overset{-}{B}F_3 \ + \ H^+ \xrightarrow{\Delta H_{diss}} CH_2=CH-O^- \ + \ BF_3 \ + \ H^+$$

Scheme 7

3-aminoquinoline to 317 kcal mol^{-1} for deprotonated 2,4,6-trihydroxyaceto-phenone. In addition, Kenttämaa and co-workers[136] explored the acidity and recombination energy of the adenine radical cation. Bracketing experiments in an FT-ICR indicate a ΔH_{acid} of 221 kcal mol^{-1} and an electron recombination energy of 8.55 eV. These thermochemical data suggest that the adenine radical cation will react by different pathways with guanine (electron transfer or proton transfer), cytosine (proton transfer) and thymine (no reactivity). As a part of their work on borazine, Chiavarino and co-workers[78] reported a gas phase basicity (185 kcal mol^{-1}) and acidity (365 kcal mol^{-1}) for this novel molecule. Abboud and co-workers[137] have used a variety of techniques to study the protonation of 3-nitropyrazole and 4-nitropyrazole. They find that protonation is preferred on the ring nitrogen and obtained gas phase basicity values of 199 and 201 kcal mol^{-1}, respectively, for the two heterocycles. Decker, Adams, and Babcock[93] reported on the acidity of the radical cation of HSSH. Using a SIFT to bracket the acidity, they determined a ΔH_{acid} of 178 kcal mol^{-1}. Cacace and co-workers[98] reported a proton affinity of 150 kcal mol^{-1} for CH_2Cl_2. Finally, Nibbering and co-workers[138] have shown that an endoergic proton transfer from protonated naphthalene can be accomplished by photoexcitation of the cation in an FT-ICR.

C. Complexation energies

The thermodynamics of association reactions can also be determined with high accuracy by mass spectrometry. Several studies explored the energetics of hydrogen bonding in small to medium size clusters. McMahon and co-workers[139] have used a high pressure mass spectrometer (HPMS) to complete a comprehensive study of the thermochemistry of clustering reactions involving halides ($X = F$, Cl, Br, and I) and a variety of alcohols (ROH, $R = CH_3$, CH_3CH_2, $(CH_3)_2CH$, and $(CH_3)_3C$). Enthalpy and entropy values were obtained for clusters with up to three solvent molecules and the data are modeled by computational studies. Along with trends in the complexation energies related to halide size and alcohol polarizability, the authors found a good, linear correlation between the complexation energy and the acidity difference between the alcohol and the halide. This relationship

applies for all the halides, but cyanide ion gives a different linear relationship. Chabinyc and Brauman[140] have used an FT-ICR to study the effect of anion basicity on the hydrogen bond strength of ion–molecule complexes of acetylide anions, RCC^- (R = *tert*-butyl, H, phenyl, and *p*-tolyl), with methanol. Although the acetylides vary in proton affinity over a 7 kcal mol^{-1} range (379 to 372 kcal mol^{-1}), all the hydrogen-bonded complexes with methanol have approximately the same complexation energy (-20.8 to -21.6 kcal mol^{-1}). This result is in sharp contrast to the acidity–complexation energy relationship that McMahon and co-workers found for the halide–alcohol complexes. Apparently, the relationship between the relative acidities of the complex partners and the complexation energy is not universal and depends on the nature of the system. In this case, all of the acetylides have a similar charge distribution (*i.e.*, localized carbon lone pair) and the remote substituents stabilize the bare acetylide as much as the hydrogen-bonded complex so there is no net effect on the complexation energy. Meot-Ner and co-workers[141,142] have studied the solvation energetics of two systems by HPMS. The binding energies of two quaternary ammonium ions, $(CH_3)_4N^+$ and acetylcholine ($(CH_3)_3N^+CH_2$ $CH_2O(O)CCH_3$), to neutral molecules were measured in an effort to model interactions in the acetylcholine receptor channel.[141] Binding energies to simple aromatics (*e.g.*, benzene) are similar to those to H_2O (8–10 kcal mol^{-1}), but weaker than those to polar organic molecules such as esters (12–15 kcal mol^{-1}) and amides (20 kcal mol^{-1}). The authors argue that these results provide a foundation for understanding the role of aromatic residues in the acetylcholine receptor channel. The work is supported by extensive computational modeling. In a second paper, Meot-Ner and co-workers[141] have completed a comprehensive study of cluster formation involving three charge carriers (proton, acetate, and hydroxide) with two solvates (acetic acid and water). Complexation energies were reported for numerous combinations and the effects of aggregation (*i.e.*, formation of acetic acid dimers) on the acidity and basicity of the clustered species were analyzed. Meot-Ner and co-workers[143] have also studied the formation of the trimethylsulfonium ion and set a lower limit on the enthalpy of its formation on the basis of data from the clustering reactions of dimethyl sulfide with carbocations. Ryzhov and Dunbar[144] have used direct association equilibria in an FT-ICR to determine the hydration enthalpy of protonated 18-crown-6 (28.3 kcal mol^{-1}). The results are consistent with those from an earlier HPMS study, but could be obtained at much lower temperatures. Williamson and Creaser[145] have studied the stabilities of complexes between protonated amines RNH_3^+ [R = $CH_3(CH_2)_2$, $C_6H_5(CH_2)_2$, and $O_2NC_6H_4$ $(CH_2)_2$] and crown ethers in an ion trap mass spectrometer. The qualitative results suggest that the addition of an aromatic ring to the crown or to the amine reduces the stability of the complex. Finally, Milligan *et al.*[146] have used an FT-ICR and a SIFT to examine the rates of complex formation in the reactions of protonated and ionized acrylonitrile with neutral acrylonitrile.

Acknowledgement

References

1 N. M. M. Nibbering, S. Ingemann and L. J. de Koning, in *The Structure, Energetics and Dynamics of Organic Ions*, T. Baet, C. Y. Ng and I. Powis, Eds., Wiley & Sons, New York, 1996.
2 S. Fornarini, *Mass Spectrom. Rev.*, 1997, **15**, 365.
3 S. Fornarini and M. E. Crestoni, *Acc. Chem. Res.*, 1998, **31**, 827.
4 M. L. Chabinyc, S. L. Craig, C. K. Regan and J. I. Brauman, *Science*, 1998, **279**, 1882.
5 M. Born, S. Ingemann and N. M. M. Nibbering, *Mass Spectrom. Rev.*, 1997, **16**, 181.
6 A. A. Viggiano, S. T. Arnold and R. A. Morris, *Int. Rev. Phys. Chem.*, 1998, **17**, 147.
7 C. Lifshitz, *Mass Spectrom. Rev.*, 1993, **12**, 261.
8 D. K. Bohme, *Can. J. Chem.*, 1999, **77**, 1453.
9 O. Bortolini and M. Fogagnolo, *Mass Spectrom. Rev.*, 1995, **14**, 117.
10 R. Damrauer and J. A. Hankin, *Chem. Rev.*, 1995, **95**, 1137.
11 J. A. Stone, *Mass Spectrom. Rev.*, 1997, **16**, 25.
12 M. Sablier and C. Roland, *Mass Spectrom. Rev.*, 1993, **12**, 285.
13 D. Smith and P. Spanël, *Mass Spectrom. Rev.*, 1995, **14**, 255.
14 S. J. Blanksby and J. H. Bowie, *Mass Spectrom. Rev.*, 1999, **18**, 131.
15 J. S. Brodbelt, *Mass Spectrom. Rev.*, 1997, **16**, 91.
16 M. K. Green and C. B. Lebrilla, *Mass Spectrom. Rev.*, 1997, **16**, 53.
17 W. Lindinger, A. Hansel and A. Jordan, *Chem. Soc. Rev.*, 1998, **27**, 347.
18 D. Schroder and H. Schwarz, *J. Phys. Chem. A*, 1999, **103**, 7385.
19 S. Gronert, *J. Mass Spectrom.*, 1999, **34**, 787.
20 C. S. Hoaglund-Hyzer, A. E. Counterman and D. E. Clemmer, *Chem. Rev.*, 1999, **99**, 3037.
21 G. V. Karachevtsev and P. S. Vinogradov, *Usp. Khim.*, 1999, **68**, 605.
22 M. Tsuji, T. Arikawa and Y. Nishimura, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 293.
23 A. A. Mosi, W. R. Cullen and G. K. Eigendorf, *Int. J. Mass Spectrom.*, 1999, **191**, 195.
24 A. A. Mosi, R. H. Skelton and G. K. Eigendorf, *J. Mass Spectrom.*, 1999, **34**, 1274.
25 R. C. Dunbar, J. Shen, E. Melby and G. A. Olah, *J. Am. Chem. Soc.*, 1973, **95**, 7200.
26 M. Satterfield and J. S. Brodbelt, *J. Am. Soc. Mass Spectrom.*, 1999, **10**, 209.
27 B. Chiavarino, M. E. Crestoni and S. Fornarini, *J. Am. Chem. Soc.*, 1999, **121**, 2619.
28 N. J. Oldham, *Rapid Commun. Mass Spectrom.*, 1999, **15**, 1694.
29 G. Moneti, G. Pieraccini, D. Favretto and P. Traldi, *J. Mass Spectrom.*, 1998, **33**, 1148.
30 N. J. Oldham and A. Svatos, *Rapid Commun. Mass Spectrom.*, 1999, **13**, 331.
31 L. A. B. Moraes, T. Kotiaho and M. N. Eberlin, *J. Mass Spectrom.*, 1999, **34**, 670.
32 L. A. B. Moraes and M. N. Eberlin, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2105.
33 L. A. B. Moraes, F. C. Gozzo, M. N. Eberlin and P. Vainiotalo, *J. Org. Chem.*, 1997, **62**, 5096.
34 M. Sharifi and J. Einhorn, *Int. J. Mass Spectrom.*, 1999, **191**, 253.
35 O. Bortolini, L. Pandolfo, C. Tomaselli and P. Traldi, *Int. J. Mass Spectrom.*, 1999, **191**, 171.
36 J. L. M. Abboud, M. Herreros, R. Notario, J. S. Lomas, J. Mareda and P. Muller, *J. Org. Chem.*, 1999, **64**, 6401.
37 H. Flores, J. Z. Davalos, J. L. M. Abboud, O. Castano, R. Gomperts and P. Jimenez, *J. Phys. Chem. A*, 1999, **103**, 7555.
38 T. A. Shaler, D. Borchardt and T. H. Morton, *J. Am. Chem. Soc.*, 1999, **121**, 7907.
39 A. Nixdorf and H. F. Grützmacher, *Eur. Mass Spectrom.*, 1999, **5**, 93.
40 E. D. Nelson, S. E. Tichy and H. I. Kenttämaa, *J. Chem. Soc. Perkin Trans. 2*, 1999, 2267.
41 R. Thissen, O. Dutuit, H. E. Audier and P. Mourgues, *J. Mass Spectrom.*, 1999, **34**, 850.
42 W. N. Olmstead and J. I. Brauman, *J. Am. Chem. Soc.*, 1977, **99**, 4219.
43 W. L. Hase, H. Wang and G. H. Peslherbe, *Adv. Gas Phase Ion Chem.*, 1998, **3**, 125.
44 G. S. Li and W. L. Hase, *J. Am. Chem. Soc.*, 1999, **121**, 7124.
45 K. M. Ervin, *Int. J. Mass Spectrom.*, 1999, **187**, 343.
46 S. L. Craig, M. L. Zhong and J. I. Brauman, *J. Am. Chem. Soc.*, 1999, **121**, 11790.
47 (*a*) P. Ayotte, J. Kim, J. A. Kelley, S. B. Nielsen and M. A. Johnson, *J. Am. Chem. Soc.*, 1999, **121**, 6950; (*b*) L. Lehmann and E. Illenberger, *Int. J. Mass Spectrom.*, 1999, **187**, 463.

48 S. L. Craig and J. I. Brauman, *J. Am. Chem. Soc.*, 1999, **121**, 6690.
49 J. M. Hevko, S. Dua, M. S. Taylor and J. H. Bowie, *Int. J. Mass Spectrom.*, 1999, **187**, 327.
50 J. M. Hevko, S. Dua, J. H. Bowie and M. S. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1999, 457.
51 A. E. Flores and S. Gronert, *J. Am. Chem. Soc.*, 1999, **121**, 2627.
52 S. Gronert and J. Azebu, *Org. Lett.*, 1999, **1**, 503.
53 S. Gronert and L. M. Fong, *Int. J. Mass Spectrom.*, 1999, **192**, 185.
54 A. Filippi and M. Speranza, *Int. J. Mass Spectrom.*, 1999, **187**, 425.
55 G. Renzi, A. Lombardozzi, E. Dezi, A. Pizzabiocca and M. Speranza, *Chem. Eur. J.*, 1996, **2**, 316.
56 E. Dezi, A. Lombardozzi, G. Renzi, A. Pizzabiocca and M. Speranza, *Chem. Eur. J.*, 1996, **2**, 323.
57 B. T. Frink and C. M. Hadad, *J. Chem. Soc., Perkin Trans. 2*, 1999, 2397.
58 M. L. Zhong and J. I. Brauman, *J. Am. Chem. Soc.*, 1999, **121**, 2508.
59 B. D. Wladkowski, J. L. Wilbur and J. I. Brauman, *J. Am. Chem. Soc.*, 1994, **116**, 2471.
60 A. Artau, Y. Ho, H. Kenttämaa and R. R. Squires, *J. Am. Chem. Soc.*, 1999, **121**, 7130.
61 J. C. Sheldon, M. S. Taylor, J. H. Bowie, S. Dua, C. S. B. Chia and P. C. H. Eichinger, *J. Chem. Soc., Perkin Trans. 2*, 1999, 333.
62 R. A. Seburg, B. T. Hill and R. R. Squires, *J. Chem. Soc., Perkin Trans. 2*, 1999, 2249.
63 R. A. Seburg, B. T. Hill, R. A. Jesinger and R. R. Squires, *J. Am. Chem. Soc.*, 1999, **121**, 6310.
64 W. L. Karney and W. T. Borden, *J. Am. Chem. Soc.*, 1997, **119**, 1378.
65 K. M. Broadus and S. R. Kass, *J. Chem. Soc., Perkin Trans. 2*, 1999, 2389.
66 R. A. Morris, T. M. Miller, J. F. Paulson, A. A. Viggiano, M. T. Feldmann and R. A. King, *J. Chem. Phys.*, 1999, **110**, 8436.
67 S. Kato, C. H. DePuy, S. Gronert and V. M. Bierbaum, *J. Am. Soc. Mass Spectrom.*, 1999, **10**, 840.
68 E. D. Nelson, R. M. Li and H. I. Kenttämaa, *Int. J. Mass Spectrom.*, 1999, **187**, 91.
69 (*a*) P. Gerbaux, M. Barbieux-Flammang, Y. Van Haverbeke and R. Flammang, *Rapid Commun. Mass Spectrom.*, 1999, **13**, 1707; (*b*) P. Gerbaux, Y. Van Haverbeke and R. Flammang, *Int. J. Mass Spectrom.*, 1999, **184**, 39.
70 K. K. Thoen and H. I. Kenttämaa, *J. Am. Chem. Soc.*, 1999, **121**, 800.
71 B. T. Hill, J. C. Poutsma, L. J. Chyall, J. Hu and R. R. Squires, *J. Am. Soc. Mass Spectrom.*, 1999, **10**, 896.
72 Y. Ling, G. K. Koyanagi, D. Caraiman, V. Baranov and D. K. Bohme, *Int. J. Mass Spectrom.*, 1999, **183**, 349.
73 Y. Ling, G. K. Koyanagi, D. Caraiman, A. C. Hopkinson and D. K. Bohme, *Int. J. Mass Spectrom.*, 1999, **192**, 215.
74 R. K. Milburn, A. C. Hopkinson, J. Sun and D. K. Bohme, *J. Phys. Chem. A.*, 1999, **103**, 7528.
75 R. L. DeLeon, C. P. Dufresne, E. F. Rexer and J. F. Garvey, *Int. J. Mass Spectrom.*, 1999, **187**, 149.
76 X. H. Guo and H. F. Grützmacher, *J. Am. Chem. Soc.*, 1999, **121**, 4485.
77 L. Ma, Z. Y. Liu, W. J. Wang, X. H. Guo and S. Y. Liu, *J. Phys. Chem. A.*, 1999, **103**, 8634.
78 B. Chiavarino, M. E. Crestoni, A. Di Marzio and S. Fornarini, *J. Am. Chem. Soc.*, 1999, **121**, 11204.
79 F. Wang, W. A. Tao, F. C. Gozzo, M. N. Eberlin and R. G. Cooks, *J. Org. Chem.*, 1999, **64**, 3213.
80 M. N. Eberlin and R. G. Cooks, *Org. Mass Spectrom.*, 1993, **28**, 679.
81 W. G. A. Tao, F. Wang, J. W. Denault and R. G. Cooks, *J. Chem. Soc., Perkin Trans. 2*, 1999, 2325.
82 D. Leblanc, H. E. Audier and J. P. Denhez, *J. Mass Spectrom.*, 1999, **34**, 969.
83 T. A. Kochina, D. V. Vrazhnov, I. S. Ignat'ev, V. D. Nefedov and E. N. Sinotova, *Russ. J. Gen. Chem.*, 1999, **69**, 905.
84 H. Ishikawa, J. Hashimoto, Y. Shimanuki and N. Mikami, *J. Phys. Chem. A*, 1999, **103**, 2007.
85 P. Antoniotti, C. Canepa, L. Operti, R. Rabezzana, G. Tonachini and G. A. Vaglio, *J. Phys. Chem. A.*, 1999, **103**, 10945.
86 P. Antoniotti, L. Operti, R. Rabezzana, G. A. Vaglio and P. Volpe, *Int. J. Mass Spectrom.*, 1999, **191**, 243.
87 P. Antoniotti, C. Canepa, L. Operti and R. Rabezzana, *J. Organomet. Chem.*, 1999, **589**, 150.
88 L. E. Ramirez-Arizmendi, Y. Q. Yu and H. I. Kenttämaa, *J. Am. Soc. Mass Spectrom.*, 1999, **10**, 379.
89 F. Wang, S. G. Ma, W. A. Tao and R. G. Cooks, *Angew. Chem., Int. Ed.*, 1999, **38**, 386.
90 J. F. Gal, M. Herreros, P. C. Maria, L. Operti, C. Pettigiani and R. Rabezzana, *J. Mass Spectrom.*, 1999, **34**, 1296.
91 R. Sparrapan, M. A. Mendes and M. N. Eberlin, *Int. J. Mass Spectrom.*, 1999, **183**, 369.
92 O. Bortolini, A. Guerrini, V. Lucchini, G. Modena and L. Pasquato, *Tetrahedron Lett.*, 1999, **40**, 6073.
93 B. K. Decker, N. G. Adams and L. M. Babcock, *Int. J. Mass Spectrom.*, 1999, **187**, 727.
94 P. Gerbaux, R. Flammang, C. T. Pedersen and M. W. Wong, *J. Phys. Chem. A*, 1999, **103**, 3666.
95 D. Lahem, R. Flammang, H. T. Le, T. L. Nguyen and M. T. Nguyen, *J. Chem. Soc., Perkin Trans. 2*, 1999, 821.
96 R. Flammang, P. Gerbaux, M. Barbieux-Flammang, C. T. Pedersen and A. T. Bech, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1683.
97 G. N. Merrill, U. Zoller, D. R. Reed and S. R. Kass, *J. Org. Chem.*, 1999, **64**, 7395.
98 F. Cacace, G. de Petris, F. Pepi, M. Rosi and A. Troiani, *Chem. Eur. J.*, 1999, **5**, 2750.

99 G. de Petris, F. Pepi and M. Rosi, *Chem. Phys. Lett.*, 1999, **304**, 191.

100 L. S. Nichols and A. J. Illies, *Int. J. Mass Spectrom.*, 1999, **187**, 413.

101 L. S. Nichols and A. J. Illies, *J. Am. Chem. Soc.*, 1999, **121**, 9176.

102 G. B. I. Scott, D. A. Fairley, C. G. Freeman, M. J. McEwan and V. G. Anicich, *J. Phys. Chem. A.*, 1999, **103**, 1073.

103 G. B. I. Scott, D. A. Fairley, D. B. Milligan, C. G. Freeman and M. J. McEwan, *J. Phys. Chem. A*, 1999, **103**, 7470.

104 M. J. McEwan, G. B. I. Scott, N. G. Adams, L. M. Babcock, R. Terzieva and E. Herbst, *Astrophys. J.*, 1999, **513**, 287.

105 D. A. Fairley, D. B. Milligan, L. M. Wheadon, C. G. Freeman, R. G. A. R. Maclagan and M. J. McEwan, *Int. J. Mass Spectrom.*, 1999, **187**, 253.

106 S. T. Arnold, S. Williams, I. Dotan, A. J. Midey, R. A. Morris and A. A. Viggiano, *J. Phys. Chem. A*, 1999, **103**, 8421.

107 V. Le Page, Y. Keheyan, T. P. Snow and V. M. Bierbaum, *Int. J. Mass Spectrom.*, 1999, **187**, 949.

108 V. Le Page, Y. Keheyan, T. P. Snow and V. M. Bierbaum, *J. Am. Chem. Soc.*, 1999, **121**, 9435.

109 J. R. Vacher, E. Le Duc and M. Fitaire, *Planet. Space Sci.*, 1999, **47**, 151.

110 V. N. Fishman, S. T. Graul and J. J. Grabowski, *Int. J. Mass Spectrom.*, 1999, **187**, 477.

111 V. N. Fishman and J. J. Grabowski, *J. Phys. Chem. A*, 1999, **103**, 4879.

112 T. L. Williams, L. M. Babcock and N. G. Adams, *Int. J. Mass Spectrom.*, 1999, **187**, 759.

113 E. R. Lovejoy, *Int. J. Mass Spectrom.*, 1999, **191**, 231.

114 J. M. Thomas and A. A. Viggiano, *J. Phys. Chem. A*, 1999, **103**, 2720.

115 P. Spanël and D. Smith, *Int. J. Mass Spectrom.*, 1999, **184**, 175.

116 P. Spanël and D. Smith, *Int. J. Mass Spectrom.*, 1999, **189**, 213.

117 P. Spanël and D. Smith, *Int. J. Mass Spectrom.*, 1999, **187**, 139.

118 D. A. Fairley, D. B. Milligan, C. G. Freeman, M. J. McEwan, P. Spanël and D. Smith, *Int. J. Mass Spectrom.*, 1999, **193**, 35.

119 D. Smith, P. Spanël, T. A. Holland , W. A. Singari and J. B. Elder, *Rapid Commun. Mass Spectrom.*, 1999, **13**, 724.

120 P. Spanël, S. Davies and D. Smith, *Rapid Commun. Mass Spectrom.*, 1999, **13**, 1733.

121 P. Spanël and D. Smith, *Rapid Commun. Mass Spectrom.*, 1999, **13**, 585.

122 P. Spanël, D. Smith, T. A. Holland , W. Al Singary and J. B. Elder, *Rapid Commun. Mass Spectrom.*, 1999, **13**, 1354.

123 C. Warneke, T. Karl, H. Judmaier, A. Hansel, A. Jordan, W. Lindinger and P. J. Crutzen, *Global Biogeochem. Cycles*, 1999, **13**, 9.

124 R. Fall, T. Karl, A. Hansel, A. Jordan and W. Lindinger, *J. Geophys. Res.-Atmos.*, 1999, **104**, 15963.

125 R. Holzinger, C. Warneke, A. Hansel, A. Jordan and W. Lindinger, *Geophys. Res. Lett.*, 1999, **26**, 1161.

126 A. Boschetti, F. Biasioli, M. van Opergen, C. Warneke, A. Jordan, R. Holzinger, P. Prazeller, T. Karl, A. Hansel, W. Lindinger and S. Iannotta, *Postharvest Biol. Technol.*, 1999, **17**, 143.

127 A. Hansel, A. Jordan, C. Warneke, R. Holzinger, A. Wisthaler and W. Lindinger, *Plasma Sources Sci. Technol.*, 1999, **8**, 332.

128 T. Reiner, O. Mohler and F. Arnold, *J. Geophys. Res.-Atmos.*, 1999, **104**, 13943.

129 J. Berkowitz, G. B. Ellison and D. Gutman, *J. Phys. Chem. A*, 1994, **98**, 2744.

130 K. M. Broadus and S. R. Kass, *Int. J. Mass Spectrom.*, 1999, **187**, 179.

131 J. H. Ren, C. J. Cramer and R. R. Squires, *J. Am. Chem. Soc.*, 1999, **121**, 2633.

132 K. Norrman and T. B. McMahon, *J. Phys. Chem. A*, 1999, **103**, 7008.

133 S. P. de Visser, E. van der Horst, L. J. de Koning, W. J. van der Hart and N. M. M. Nibbering, *J. Mass Spectrom.*, 1999, **34**, 303.

134 K. Breuker, R. Knochenmuss and R. Zenobi, *J. Am. Soc. Mass Spectrom.*, 1999, **10**, 1111.

135 K. Breuker, R. Knochenmuss and R. Zenobi, *Int. J. Mass Spectrom.*, 1999, **184**, 25.

136 C. T. Hwang, C. L. Stumpf, Y. Q. Yu and H. I. Kenttämaa, *Int. J. Mass Spectrom.*, 1999, **183**, 253.

137 J. L. M. Abboud, R. Notario, M. Yanez, O. Mo and R. Flammang, *J. Phys. Org. Chem.*, 1999, **12**, 787.

138 F. H. W. van Amerom, W. J. van der Hart and N. M. M. Nibbering, *Int. J. Mass Spectrom.*, 1999, **183**, 7.

139 B. Bogdanov, M. Peschke, D. S. Tonner, J. E. Szulejko and T. B. McMahon, *Int. J. Mass Spectrom.*, 1999, **187**, 707.

140 M. L. Chabinyc and J. I. Brauman, *J. Phys. Chem. A*, 1999, **103**, 9163.

141 C. A. Deakyne and M. Meot-Ner, *J. Am. Chem. Soc.*, 1999, **121**, 1546.

142 M. M. N. Meot-Ner, D. E. Elmore and S. Scheiner, *J. Am. Chem. Soc.*, 1999, **121**, 7625.

143 C. A. Deakyne, D. M. Knuth, M. Meot-Ner, C. M. Breneman and J. F. Liebman, *J. Mol. Struct.*, 1999, **486**, 33.

144 V. Ryzhov and R. C. Dunbar, *J. Am. Soc. Mass Spectrom.*, 1999, **10**, 862.

145 B. L. Williamson and C. S. Creaser, *Int. J. Mass Spectrom.*, 1999, **188**, 53.

146 D. B. Milligan, P. F. Wilson, M. J. McEwan and V. G. Anicich, *Int. J. Mass Spectrom.*, 1999, **187**, 663.