REVIEW COMMENTARY

PROBING ONIUM IONS AND CARBOCATIONS BY DESORPTION/IONIZATION MASS SPECTROMETRY: CROSSING THE THRESHOLD BETWEEN FRAGILE SALTS AND GASEOUS INTACT CATIONS AND SUBSEQUENT GUEST–HOST AND CATION–MOLECULE CLUSTER CHEMISTRY

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The utility of desorption/ionization mass spectrometric (DI/MS) techniques in dealing with physical organic problems involving fragile onium salts and carbocation salts has been explored. The efficacy of these methods, especially when coupled to tandem mass spectrometry, goes much beyond the analytical aspects dealing with identity/purity determinations. For example, insight can be gained regarding the role of the counterion in subsequent cation decomposition pathways. Guest–host chemistry of onium ions and various hosts (crowns, calixarenes) can be probed. The decomposition chemistry of the resulting ion–molecule clusters can be studied. Examples of onium salts and carbocation salts that have been studied are few, probably because research in this area has been mainly a domain for analytical chemists. This paper calls attention to the possibilities for dealing with topical physical organic problems.

INTRODUCTION

The intention here is to demonstrate to those interested in preparing and characterizing organic cation salts the potential that desorption/ionization mass spectrometry (DI/MS), fast atom bombardment (FAB), field desorption (FD), secondary ion mass spectrometry (SIMS), californium plasma desorption (^{252}Cf-PDMS) and laser desorption (LDMS) can offer in studies of onium ions and carbocation salts.

A second goal is to highlight the efficacy of the techniques in probing the guest–host chemistry of onium ions in the gas phase. In such instances, parallel solution and gas-phase studies can yield useful clues as to the role of solvation.

A discussion of DI/MS methods is beyond the scope of this paper. There has been an overwhelming amount of research in this area, and numerous lead reviews and monographs exist.[1,2]

Many carbocations and onium (or enium) ions can be cleanly generated in the mass spectrometer by ion–molecule reactions and used as electrophiles in a subsequent reaction whose products can be identified by tandem mass spectrometry.[3] However, FAB and FD allow cation salts synthesized in the laboratory to be transferred into the gas phase (usually from a liquid matrix) for direct study. This approach can have several advantages:

(1) The methods provide a complementary analytical technique for the determination of the molecular mass and purity of numerous cation salts. Many onium salts, and especially carbocation salts, are very hygroscopic, and microanalysis is not always feasible. This often leaves NMR spectrometry as the only identification tool. The higher sensitivity of MS compared with NMR can be advantageous, pointing to the power of the desorption/ionization method as a complementary tool in preparative ion chemistry.

(2) The influence of the counterion (its structure and nucleophilicity) on the cation reactivity can be assessed by using DI/MS techniques such as FAB and FD, in which two cation/one anion cluster ions are usually formed. Also, the counterions can be examined more

closely by negative ion mass spectrometry. NMR data often do not contain this type of information, although a *slight counterion* dependence of NMR chemical shifts can be seen in various classes of onium ions.[4]

(3) Once in the gas phase, the chemistry of the ion–molecule cluster can be probed by collisional activation decomposition (CAD), using a tandem mass spectrometer.

(4) The approach provides a means to study the guest–host chemistry of the desorbed cation (with crown ethers, azacrowns, lariat ethers, suitable calixarenes and cyclodextrins) for comparison with solution studies in which guest–host interactions are usually probed by NMR titration and kinetic studies. Whereas solid-state structures of a number of ammonium, phosphonium, hydronium and diazonium cations complexed to 18-crown-6 have been determined,[5] parallel gas-phase complexation studies probing guest-host interactions are only beginning to emerge.

(5) The guest-host chemistry of fragment ions derived from the original onium ion or carbocation salts can also be examined.

(6) Recent synthetic design of perfluorinated crowns and cryptands for binding negative ions[6,7] creates opportunities to explore the complexation of low nucleophilicity gegenions (triflate, nonaflate, fluorosulfate) with such hosts in the negative ion mode. Gas-phase complexation of F^- and O_2 with perfluorinated cryptands has already been shown.[8a] Such a reduction in counterion interaction with the onium ion or *carbocation by* complexation may increase the cation electrophilic power, just as the nucleophilicity of F^- is dramatically increased by complexation of its cation with crown ethers. Counterion effects on solution complexation of ammonium salts with simple crowns have been shown by Doxsee;[8b] 2 : 1 complexes have been observed in solution.

(7) Gas-phase studies of guest–host cluster ions provide a means of probing higher order clusters (e.g. two guest/one host or two host/one guest clusters). CAD experiments allow the decomposition chemistry of higher order clusters to be probed and compared with the 1 : 1 cation–molecule clusters.

(8) It is possible to measure binding selectivities in competitive experiments where two onium ions may compete for a given host or where two hosts are allowed to complex an onium ion.

The section below provides highlights of the range of synthetically accessible onium(enium) and carbocation salts which are, in principle, amenable to DI/MS studies [In cases where the salt is very hygroscopic, a dilute solution (in acetonitrile or methylene chloride) can be prepared under nitrogen and a drop transferred quickly on to the probe tip; if a matrix is to be used, it should be anhydrous]. The subsequent section explores the characteristic features of few classes of such cation salts.

SYNTHETICALLY ACCESSIBLE ONIUM (ENIUM), CARBOCATION AND DICATION SALTS FOR DI/MS STUDIES

Onium (and enium) salts

Meerwein's early studies[9] provided the means for the preparation, isolation and characterization of a large number of onium cation salts (Meerwein salts). With the development of superacid methodology by Olah and co-workers since the 1960s, the scope of preparative onium ion and carbocation chemistry has been greatly enhanced, allowing the synthesis and characterization of more fragile, highly reactive salts. The work of numerous other contributors has further advanced the boundaries of preparative onium (enium) and carbocation chemistry.

In the area of stable onium ion salts, much activity has centred around onium ions of chalcogen centers (oxonium, sulfonium, selenonium and telluronium salts.)[12–17]

Acyclic and cyclic halonium ions have also received considerable attention. Diaryliodonium salts were the earliest class of stable iodonium salts to be isolated.[18]

Synthetic methods developed by Olah and co-workers allow the isolation of much less stable halonium salts such as Me_2Br^+ and tetramethylene bromonium salts.[11c]

Recent studies of Stang, Zefirov and co-workers have led to synthesis of useful alkynyl- and vinyliodonium salts.[19a,b] The bis(phenyliodonium)diyne and diiodonium ether salts with low nucleophilicity anions have also been synthesized.[19c–e] The preparation of the macrocyclic tetraaryltetraiodonium salt (a paraquat analogue) has been reported.[19f]

Among azonium salts, the ammonium cations are the oldest members. There is a great deal of current activity utilizing ammonium cations in guest–host chemistry in solution and in the gas phase.[20]
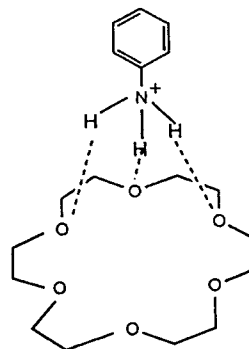
The hydrogen-bonded model shown in Figure 1 best

Figure 1. Hydrogen-bonded model for anilinium cation–crown ether interactions

describes the anilinium cation–crown ether interaction in solution.[21]

Cationic water-soluble calixarenes having trialkylammonium cation at the upper rim have been synthesized by Shinkai et al.;[22] these can serve as hosts for cations or neutral species (Figure 2).

Mono- and bis(DABCO-based)-di- and tetraammonium cationic carriers have been utilized by Li et al.[23] for nucleotide transport across organic membranes (Figure 3).

The tetracationic cyclophane cyclobis(paraquat-p-phenylene) (Figure 4) is a popular building block for [2]catananes.[24]

A number of stable azaallenium salts are known and their cyclization to 1,4-dihydroisoquinolinium salts has been demonstrated.[25]

Synthesis of nitronium and nitrosonium salts with various anions was first achieved by Hughes and Ingold

in the course of their classical studies of nitration mechanism. Their preparative aspects were much extended later by Olah et al.[26]

A wide variety of ArN_2^+ salts with different gegenions and various substituents are readily accessible. Solution complexation of ArN_2^+ with hosts and the nature of interaction have been a recent area of activity in guest–host chemistry,[27] and complementary gas-phase studies have also been performed[28,29] (see below). A modified insertion complex model, involving crown puckering and σ-base–π-acid interactions, has been proposed in solution (Figure 5).[30]

The dediazoniation (loss of N_2) mechanism for crown-complexed diazonium cations has been studied by Nakazumi et al.[31]

The history of phosphonium salts is extremely rich, owing in part to the importance of phosphonium ylides. A great variety of aryl(alkyl)phosphonium salts and their halo and hydroxy derivatives have been prepared and isolated.[32,33] The most recent examples include stable phosphonium salts of tetraphosphacubane (Figure 6).[34]
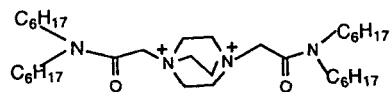
Figure 2. Trialkylammonium-substituted calixarenes as hosts
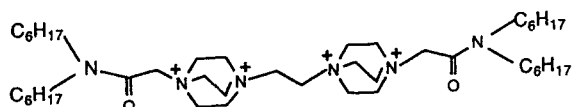
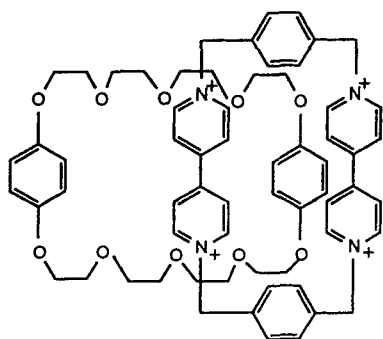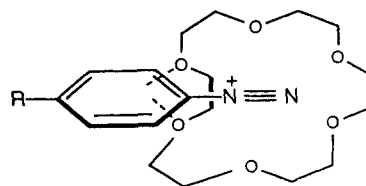Figure 3. Mono- and bis(DABCO-based)-di- and-tetraammonium cationic carriers

Figure 4. Tetracationic cyclophane cyclobis(paraquat-p-phenylene)

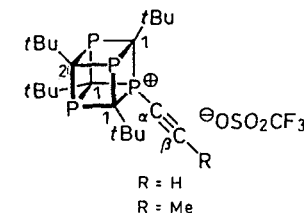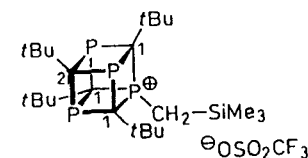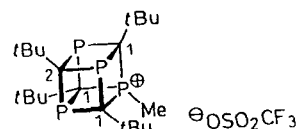Figure 5. The insertion complex model for ArN_2^+–crown guest–host cluster

Figure 6. Phosphonium salts of tetra-tert-butyltetraphosphacubane. The numbers 1 and 2 represent different types of cage carbons
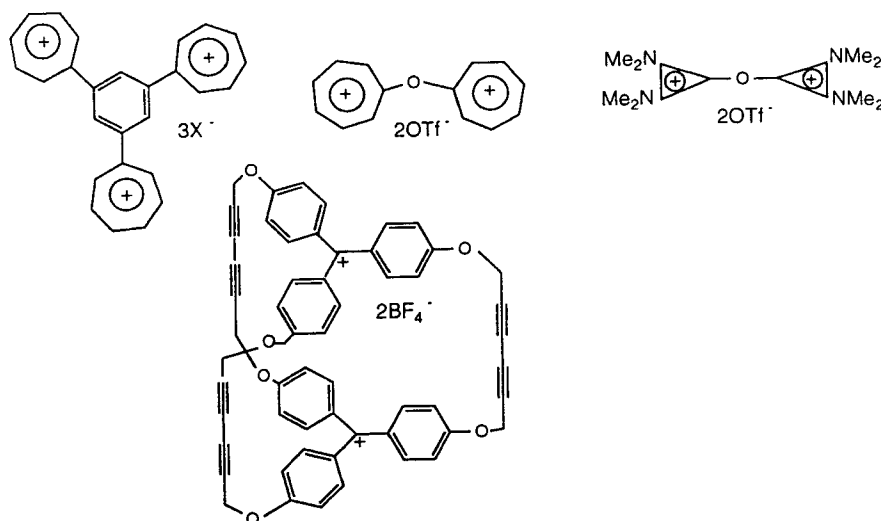
Figure 7. Examples of stable carbocation, carbodications and dication ether salts

Arsonium salts are also widely prepared and utilized synthetically as precursors to arsonium ylides. Their preparative aspects have been reviewed.[35,36]
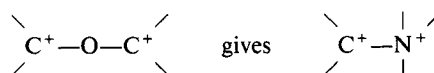
Stable carbocation, carbodication and dication ether salts

Notable examples include the adamantyl-,[10] trityl-[37] and azulene analogues of trityl cation,[38] aryl-, alkyl-, cyclopropyl-substituted tropylium,[39a] acetylium, chloro- and bromoacetylium cations,[11e] cyclopropenium[10] and t-Bu$^+$ salts.[11a] Macrocycles containing a tropylium ion unit have also been prepared.[39b] Examples for stable di- and trications are ditropylium-and tritropylium-substituted benzene,[10] numerous dication ether salts[40a] and a recently prepared triply-bridged triphenylmethyl dication (Figure 7).[40b]

The Tf$_2$O–Ph$_3$P, Tf$_2$O–HMPA and Tf$_2$O–urea systems studied by Aaberg et al.[41] provide easy access to a range of diphosphonium ether salts (Figure 8).

Extension of ketone–Tf$_2$O to enaminones as shown by Maas and co-workers gives delocalized iminium salts.[42] Nucleophilic displacement by nitrogen heterocycles on

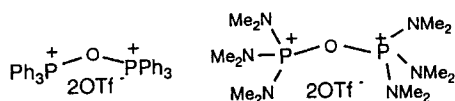$$\overset{\diagdown}{\underset{\diagup}{C^+}}\!\!-\!O\!-\!\overset{\diagup}{\underset{\diagdown}{C^+}} \qquad \text{gives} \qquad \overset{\diagdown}{\underset{\diagup}{C^+}}\!\!-\!\overset{\mid}{\underset{\mid}{N^+}}\!\!\overset{\diagup}{}$$

dications (Figure 9).[43]

Alkenediazonium salts

A number of stable alkenediazonium salts are accessible using methods developed by Bott.[44] Structural studies on alkenedizonium salts are a topic of current interest.[45]
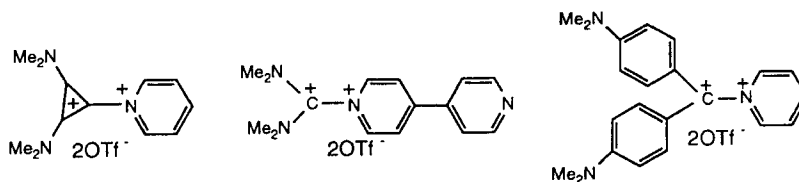

Figure 8. Stable diphosphonium ether salts

Figure 9. Examples of stable delocalized dication salts

CHARACTERISTIC FEATURES OF DI MASS SPECTRA OF ONIUM (ENIUM) IONS: WHAT CAN WE EXPECT?

Ammonium salts

Because of their higher stability relative to other onium ions, a number of investigations have dealt with their DI/MS and gas-phase guest–host studies.

Veith[46] showed that FDMS is highly suitable for $R_4N^+X^-$ salts. Apart from abundant R_4N^+ ions, cation–molecule clusters $R_4N^+ \cdot (R_4N^+X^-)_n$ ($n = 1–5$ depending on R and X) are formed. There are also cations of the type $[nR_4N^+X - 1]_n^+$ in their spectra (Figure 10).

Experiments with $Et_4N^+Br^{-1}$ (C_ABr)–$(nBu)_4N^+I^-$ (C_BI) mixture (1 : 1) shows that gegenion exchange is possible (Figure 11).
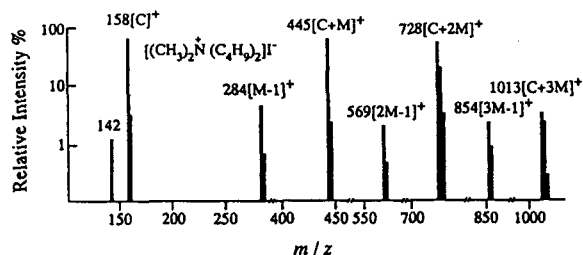

Figure 10. FD mass spectrum of $[Me_2N(nBu)_2]^+ I^-$ (C = cation; M = molecule)
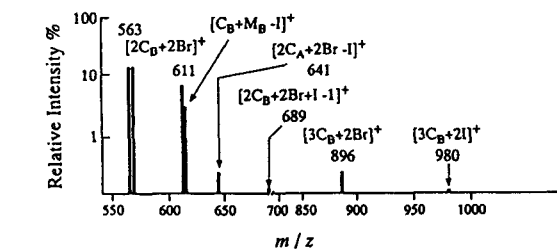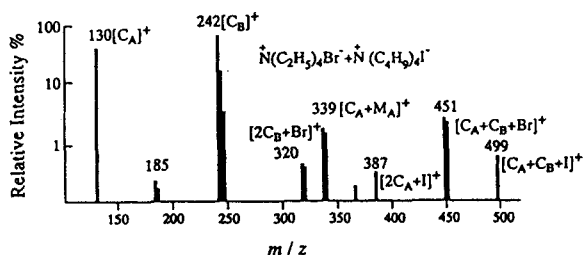

Figure 11. FD mass spectrum of $Et_4N^+Br^-$ and $(n\text{-}Bu)_4N^+I^-$ (1 : 1 mixture)

Larger ion–molecule clusters are observed at lower desorption temperatures.

The ion–molecule clusters observed with alkyl-ammonium nitrate and thiocyanate in FABMS are of the type $[(M)C]^+$, and $[(M)_nAH_x]^+$ (C = cation; A = anion; M = C^+A^-; $n = 0–6$; $x = 0–2$).[47] In the latter type of cluster ions the gegenion is protonated.

The Et_4N^+-per(3,6-anhydro)-β-cyclodextrin cluster cation (Figure 12) has been observed by FABMS (m/z 966).[20d]

Whereas low-energy CAD of ammonium–crown ether clusters leads to decomplexation and loss of ethylene oxide, high-energy CAD leads to intramolecular ring opening, forming odd-electron acyclic product ions.[20b]

Competitive binding experiments (using two different crowns) with the ammonium cation show its higher affinity for larger crowns.[20c]

Bates et al.[48a] have shown that an inclusion complex is formed between peroctylated-β-CD and NMe_4^+ in solution. Gas-phase complexation could be demonstrated by electrospray mass spectrometry.[48b]

The most recent guest–host studies between modified carbohydrates and enantiomeric ammonium cations indicate that enantioselective complexation can be seen in FABMS.[20a]

Diazonium salts

FABMS and FDMS are ideal techniques for studying diazonium ions.[28,49] With PhN_2^+ the intact cation is abundantly present. Cation–molecule clusters of the type PhN_2^+–$PhN_2^+X^-$ and doubly solvated ions $[2PhN_2^+X^- - ArN_2^+]$ are also seen, depending on the substituents on the ring. Ar^+ is a major fragment ion (Figure 13).

We have studied ArN_2^+–crown molecular complexes by FABMS and FDMS and by FAB–CAD–MS/MS.[28,29] In solution, steric crowding at the diazonium ions significantly retards or eliminates complexation; in contrast, steric effects are less stringent in
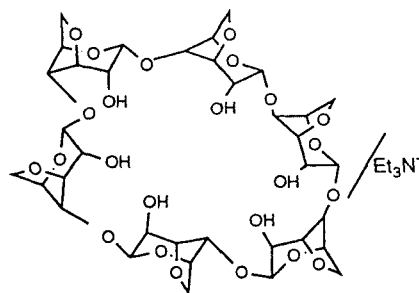

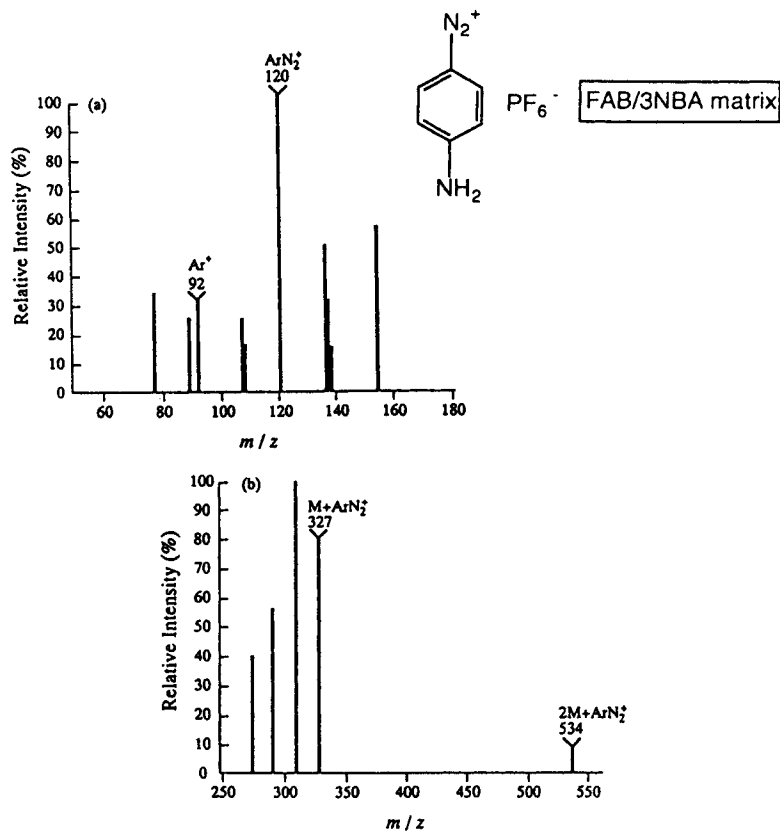Figure 12. Et_3N^+-modified β-cyclodextrin cluster ion

Figure 13. FAB mass spectrum of *p*-aminobenzenediazonium hexafluorophosphate
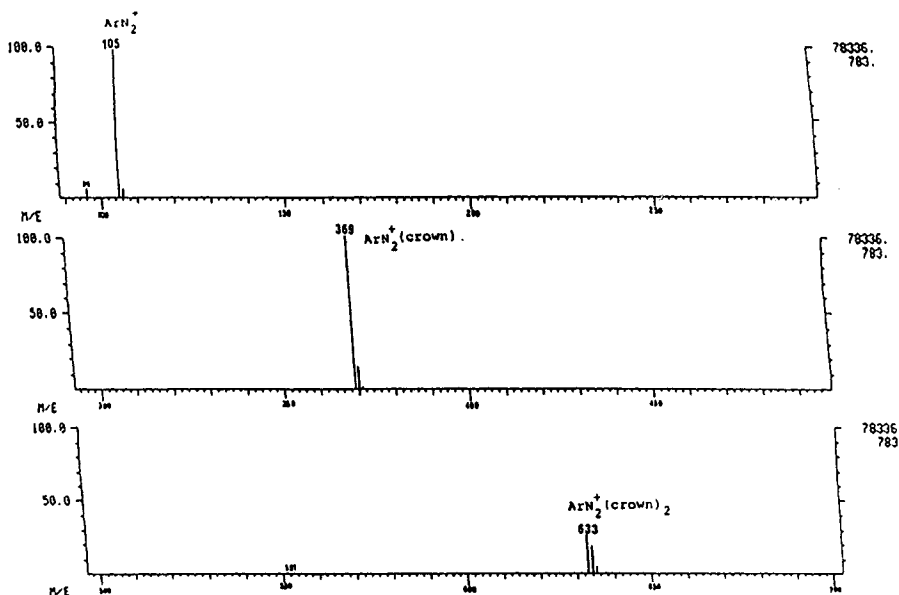
Figure 14. FD mass spectrum of benzenediazonium–18-crown-6 showing the intact ArN_2^+, the 1 : 1 complex and a 1 : 2 complex. The tiny peak at *m/z* 96 is the Schiemann product (PhF)

the gas phase. Higher order complexes such as ArN_2^+ (crown)$_2$ and ArN_2^+ (crown)$_3$ ions can be detected in some cases (Figure 14). The solution charge transfer model (σ-base–π-acid interactions) and diazonium ion encapsulation (Figure 15) provide adequate models for the observed higher order clusters.

The FAB-CAD–MS/MS experiments on ArN_2^+–crown cluster ions (Table 1) shows acid–base chemistry within the cluster.[29] Depending on the substituent, either (crown – H)$^+$ or (crown + H)$^+$ is produced in CAD spectra. With electron-withdrawing substitutents, hydride abstraction by N-β, or heterolytic dediazoniation, followed by hydride abstraction by the aryl cation, have been postulated. With activating substituents such as p-methoxy, heterolytic dediazoniation and crown protonation via expulsion of an aryne were suggested (Figure 16 and Schemes 1–3).
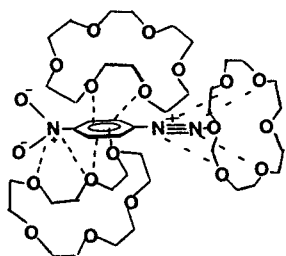

Figure 15. Hypothetical representation of an encapsulated ArN_2^+

Other azonium (azenium) salts

Despite their sensitivity to moisture and high reactivity, both $NO^+BF_4^-$ and $NO_2^+BF_4^-$ have been analysed by FABMS.[50] Apart from the cations, their ion–molecule clusters [(NO)$_2$BF$_4$]$^+$ (m/z 147) and [(NO$_2$)$_2$BF$_4$]$^+$ (m/z 163)] are also detectable.

The FABMS and FDMS methods are also applicable to the analysis of various pyrazolinium, pyrylium, thiopyrylium, pyridinium, pyrazolium and halopyrazolium salts.[51–54]

Hydrazinium salts have been examined by [252]Cf-PDMS where ion–molecule clusters are also detected.[55] With pyrazolinium salts isomeric structures can be differentiated by FABMS.[51]

Halonium ions

There are two detailed studies by Busch ad co-workers,[56,57] showing that both FABMS and SIMS are ideal for diaryliodonium salts. Intact iodonium cations are observed in abundance in every case (usually the base peak) and there is also an interesting rearrangement involving loss of neutral I$_2$ and formation of biphenyls.

Calculations show that a bent Ar—I$^+$—Ar' (or R) contributes to this process. Reduction of the aryl fragments is also observed in some cases. For example, FABMS of Ar—I$^+$—Ar' gives, apart from the molecular cation (C$^+$), ArI$^+$, [Ar—Ar]$^{+\cdot}$ and ArH$^{+\cdot}$. Since there is no reduction in the daughter ions generated by CAD of C$^+$, the reduction is not intramolecular

Table 1. FAB-CAD–MS/MS data on $ArN_2^+BF_4^-$–18-crown-6

| Substituent	Mass-selected m/z (base peak intensity)	Products [m/z (relative abundance, %)][a]		
		119	(80)	ArN_2^+
		91	(16)	Ar^+
o-Me	383 ArN_2^+ (crown) (17·96)	355	(5)	Ar^+ (crown)
		265	(19)	(crown + H)$^+$
		150	(30)	ArN_2^+
p-NO$_2$	414 ArN_2^+ (crown) (9·47)	122	(9)	Ar^+
		263	(9)	(crown – H)$^+$
p-NO$_2$	387 (ArN_2^+)$_2$BF$_4^-$ (0·82)	150	(60)	ArN_2^+
		122	(12)	Ar^+
p-Cl	403 ArN_2^+ (crown) (1·05)	111	(20)	(Ar^+)
		113	(9)	(Ar^+)
		375	(14)	Ar^+ (crown)
		377	(4)	Ar^+ (crown)
		263	(5)	Ar^+ (crown)
		135	(35)	(ArN_2^+)
p-OMe	399 ArN_2^+ (crown) (0·71)	107	(3)	(Ar^+)
		263	(3)	Ar^+crown

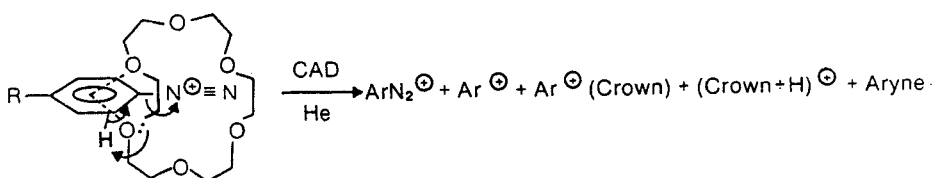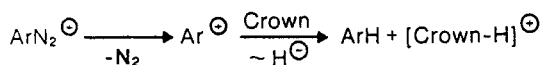[a] Tenfold sensitivity enhancement applied.
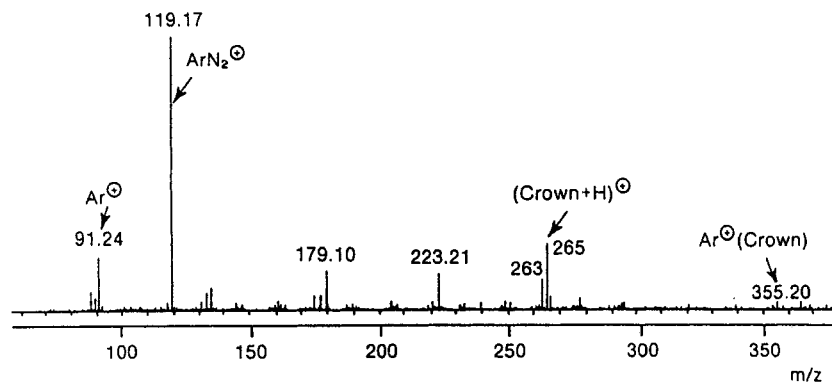
Figure 16. FAB-CAD tandem mass spectrum of o-methoxybenzenediazonium–18-crown-6 1 : 1 cluster (m/z) 383

Scheme 1. Collisionally activated dissociation of a 1 : 1 complex (heterolytic dediazoniation and crown protonation via an aryne)

Scheme 2 Collisionally induced heterolytic dediazoniation and hydride abstraction from crown by Ar^+
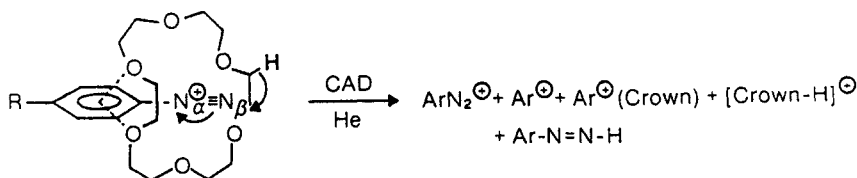
Scheme 3 Collisionally activated dissociation of a 1 : 1 complex (hydride abstraction by N-β and formation of a $(crown - H)^+$ ion)

and the matrix is the source of hydrogen. The SIMS of iodonium salt 1 (Figure 17) contains fragment ions for which reduction is observed.

Onium ions of group 16

The utility of DI/MS for analysis of various oxonium, sulfonium, selenonium and telluronium salts has been shown by our previous work.[50a] An extensive list of examples on telluronium salts was also provided by Fu et al.[58] We used FDMS, FABMS and PDMS to examine R_3O^+, R_3S^+, R_3Se^+, and R_3Te^+ salts with OTf^-, BF_4^-, $SbCl_6^-$ and I^- anions.[50]

The intact cations, two cation–one anion clusters and some fragment ions are produced. Pyrolytic decomposition products arising from apparent reaction of the anion with the cation, such as MeCl formation from $Me_3O^+SbCl_6^-$, were seen only in FDMS. Reduction in nucleophilicity of the gegenion discourages the formation of such pyrolytic products. Thus, alkyl triflates are not detected with triflate salts under the conditions where RI and RCl are formed from halides.
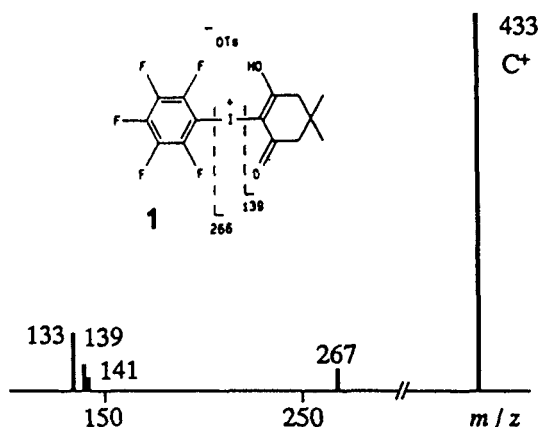
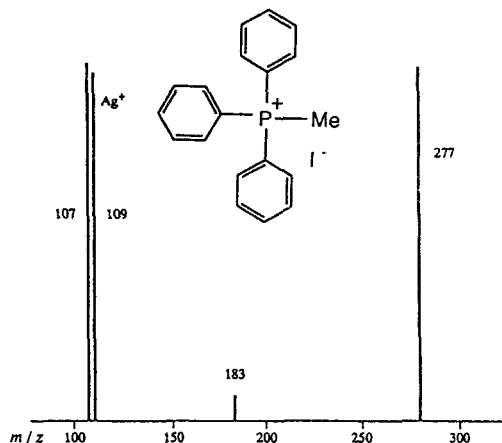Figure 17. Secondary ion mass spectrum of iodonium salt 1

Recently we have studied the guest–host chemistry of alkoxycalix [*n*]arenes with Meerwein salts.[50b] Complexation of Et₃S⁺BF₄⁻ and Et₃O⁺SbCl₆⁻ with methoxy-calix[6]arene and methoxycalix[8]arene gave 1:1 guest–host clusters (Figure 18). The calixarenes and the onium ion salts are premixed and then subjected to FABMS.

Phosphonium salts

A number of phosphonium salts have been studied by

various DI/MS methods.[59,60] FAB and SIMS provide reliable methods for detection of abundant intact cations (Figures 19 and 20). In the FAB mass spectra two cation–one anion clusters and diagnostic fragment ions are also produced.

In a recent study, we examined the *P*-methylated tetraphosphacubane (as triflate salt) by FDMS and FABMS.[59b] The intact monophosphonium ion (*m/z* 415) was observed in abundance. Complexation of the monophosphonium ion with dicyclohexano-24-crown-8

Figure 19. Secondary ion mass spectrum Ph₃P⁺MeI⁻
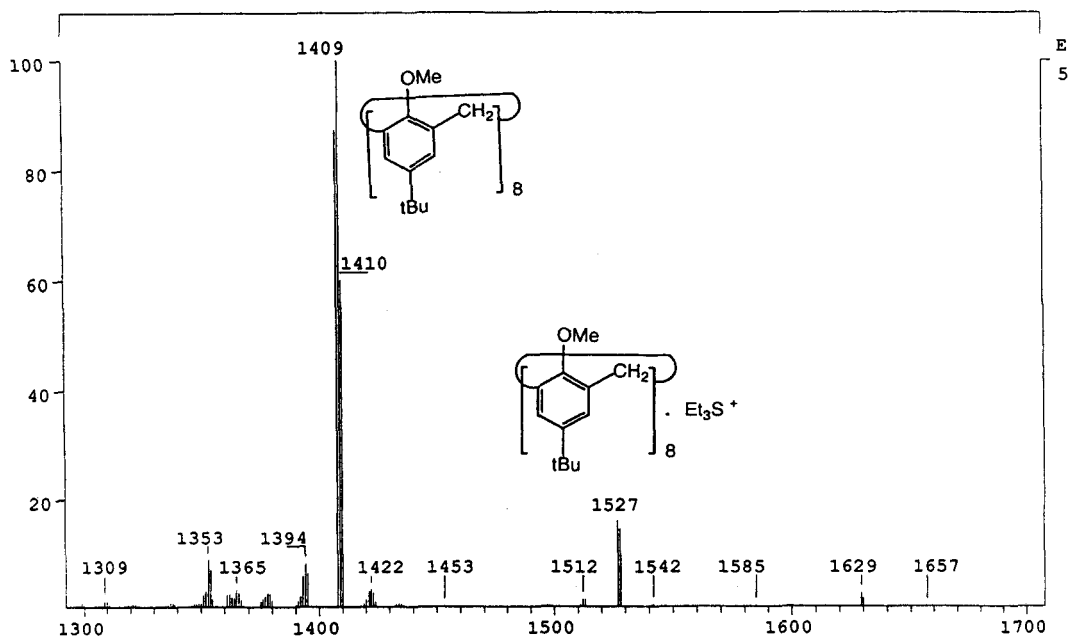
Figure 18. FAB mass spectrum of methoxycalix[8]arene–Et₃S⁺BF₄⁻ mixture
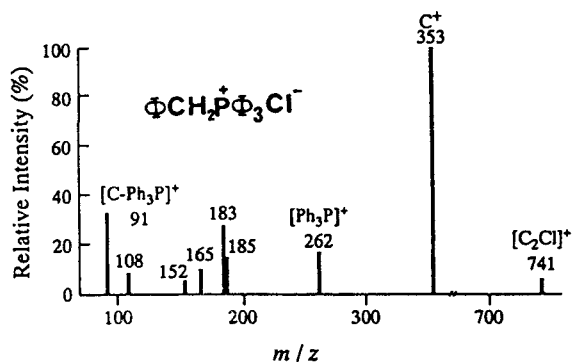
Figure 20. FAB mass spectrum of [PhCH₂PPh₃]⁺Cl⁻

was also detected (*m/z* 875) (Figure 21). MS/MS experiments on the *m/z* 415 ion (Figure 22) gave *m/z* 115 and 169 ions, assigned to *C*-methylated tBuCP and phosphirenylium cation, respectively. These fragment ions are also produced in the normal FD and FAB mass spectra of *p*-methylated tetra-*tert*-butyltetraphosphacubane and form adducts with dicyclohexano-24-crown-8. Other *P*-alkylated (alkynylated) phosphonium salts of tetraphosphacubane have also been studied by FABMS. The phosphirenylium cation (*m/z* 169) is an important common daughter ion which is produced by decomposition (FAB-CAD–MS/MS) of the intact phosphonium cations.[59b] Hence DI/MS methods are very promising in the area of novel phosphonium ions and their guest–host chemistry.

Pyridinium salts

N-Alkylpyridinium salts have been extensively studied by Katritzky and co-workers[61] using LDMS as the primary desorption technique. CAD of the intact cations led to pyridine and the corresponding carbocation. Pyridinium cations were also investigated by other groups using FABMS or FDMS.[62] There is no doubt that these methods are suitable for driving the cation into the gas phase and for subsequent ion–molecule reactions involving Py⁺. We are not aware of any gas-phase guest–host studies with pyridinium–crown systems.

Figure 21 *P*-Methylated tetraphosphacubane and its crown complexation
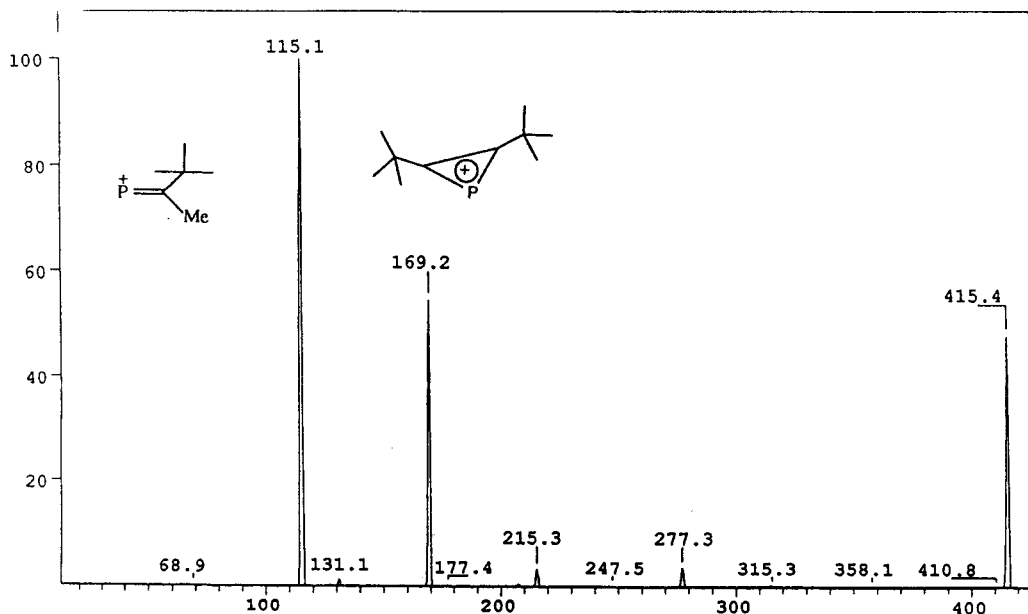
Figure 22 CAD mass spectrum of *m/z* 415 cation

CARBOCATIONS

Relatively few carbonation salts have been studied and much remains to be done. Tropylium BF_4^- and $(EtO)_3C^+BF_4^-$ were studied by FDMS by Veith.[46] Ion–molecule clusters were detected in both cases. With tropylium, a doubly solvated tropylium cation (one cation–two molecule) was also seen. We have shown[63] that FABMS and FDMS can both be utilized for studies of carbonation salts (depending on their relative stabilities). The trityl, tropylium, acetyl and adamantyl cation salts were studied. The intact cations are observable in every case but are not always the base peak.

For trifloxypropeniminium triflate salt[63] (Figure 23) the FD mass spectrum exhibits the intact cation as the
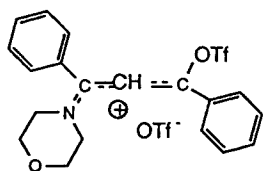

Figure 23 Trifloxypropeniminium triflate salt

base peak (m/z 426) and a two cation–one anion cluster (m/z 1001). The FAB mass spectrum shows, in addition, fragment ions due to Ph^+, morpholino cation and loss of TfOH. The latter also occurs in solution on heating of the salt in MeCN to give an alkyne salt. The PDMS data closely resemble the FAB mass spectrum.

Doubly- and multiply-charged onium salts and carbocation salts

The main problem in the detection of doubly charged cations by FABMS (or SIMS) is competing one-electron reduction, which leads, in many instances, to the detection of intact singly-charged cations. It is believed that reduction is mediated by electrons produced in the matrix.[64,65] When the charges are well separated (reduced columbic repulsion) the probability of dication detection increases.[65] Another process by which a doubly-charged dication can produce a singly-charged species is the loss of a charged fragment such as proton. FDMS appears to be more suitable than FABMS for dication detection.[66] It has been noted that LDMS is not the method of choice for dication detection.[67] Intact dications have been observed for a number of bisphosphonium ions in FAB using m-nitrobenzyl

Table 2. Examples of dication salts studied by DI/MS

Dication Studied	Method	Source	Dication Studied	Method	Source
	FDMS	Ref 66	$Ph_3\overset{+}{P}(CH_2)_4\overset{+}{P}Ph_3$ 2Br⁻	FDMS	Ref 68
	SIMS	Ref 64	$Ph_3\overset{+}{P}CH_2\text{-}C_6H_4\text{-}CH_2\overset{+}{P}Ph_3$ 2Br⁻	FDMS	Ref 65
	SIMS	Ref 66		FABMS	Ref 60
	FDMS	Ref 63		FABMS	Ref 60
				FABMS	Ref 60
	PDMS	Ref 63		FABMS	Ref 60
				FABMS	Ref 60

alcohol (m-NBA) as matrix.[60,68] Table 2 lists some diammonium, dipyridium and diphosphonium salts for which intact doubly charged cations have been observed.

With Stoddard's [2]catanane, loss of PF_6^- gegenions is observed from a singly-charged intact [2]catanane assembly in FABMS.[24]

For Vögtle's triply-bridged dication, FABMS (with m-NBA matrix) has shown $[M + H]^+$ and a cluster at m/z 956 for $[M + mO_2N(C_6H_4)CH_2O]^+$.[40b]

Onium ion binding selectivities in competitive experiments

Recent studies by Chu et al.[69] using Fourier transform ion cyclotron resonance spectrometry focused on intrinsic cation affinities and complexation of alkali metal ions with crown ethers and glymes. Work by Takahashi et al.[70] using FABMS demonstrated that for crown ethers and lariat ethers gas-phase cation affinities and solution titration methods are closely parallel. No such competitive studies have yet been reported for the onium ions ArN_2^+ and NO_2^+.

In preliminary studies[51b] we found that competitive binding with 18-crown-6 can be measured for $ArN_2^+ - Ar'N_2^+$ (1:1) by preforming the complexes in the matrix and then desorbing by FABMS. Alternatively, it should be possible to explore competition between two structurally different hosts and a given onium ion guest.

CONCLUSIONS

It has been shown that desorption/ionization mass spectrometry (especially the FAB and FD variants) offers great promise for studying fragile onium (enium) salts and carbonation salts. There is also some potential for dealing with doubly charged cations; this area needs to be explored further. The utility of DI/MS is not only from an analyst's standpoint (for purity and identity determinations), but also because it allows the desorbed cations and their fragments to be used as guests for complexation studies with crowns and calixarenes. In combination with tandem mass spectrometry, much can be learned from CAD studies which allow the chemistry of the resulting cluster ions to be explored. The higher order clusters and the forces that hold them together are fascinating subjects in guest–host chemistry. A natural progression of this line of work will be the development of more selective (complexed) electrophiles. On the other hand, the notion that gegenion interactions may be reduced by complexation with fluorinated crowns and analogues offers the potential to enhance the electrophilic reactivity of onium ions and carbonations as well.

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