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Probing Diazonium Ion – Crown Ether Molecular Complexes by Tandem Mass Spectrometry (FAB-MS/MS) Acid-Base Chemistry Within a Cluster

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Received December 27, 1989

Key Words: Diazonium ion / Crown complexation / Cluster ions / Collisional dissociation / Acid-base chemistry / Mass spectrometry

The molecular complexes (cluster ions) formed between various aromatic diazonium ion salts $\text{ArN}_2^{\oplus}\text{BF}_4^{\ominus}$ and 18-crown-6 host molecules are studied by FAB mass spectrometry. The nature of the interaction is probed by MS-MS experiments in which the ArN_2^{\oplus} (crown) 1:1 complexes are mass-selected and subjected to collisionally activated dissociation (CAD), using

helium as collision gas. The results suggest that acid-base chemistry (proton and hydride transfer) occurs within the guest – host complex. Precedented mechanistic pathways for ArN_2^{\oplus} dediazonation in the condensed phase are used as guidelines to explain these observations.

As an extension to our previously reported studies of labile carbocations, carbocations and onium ion salts by desorption/ionization mass spectrometry^{1,2}, we recently reported a study of the molecular complexes formed between aromatic diazonium ions and crown ether host molecules by field desorption (FD) and fast atom bombardment (FAB) mass spectrometry³. An examination of both *ortho* steric crowding on the diazonium ion and *peri* interactions suggested a charge transfer (CT) model for the complexation. A σ -base to π -acid argument was used to explain the observation of higher order complexes e.g. $\text{ArN}_2^{\oplus}(\text{crown})_2$ and $\text{ArN}_2^{\oplus}(\text{crown})_3$.

To provide further insight into the nature of this interaction, we have combined our FAB and FD measurements with tandem mass spectrometry. MS-MS technique has proven to be an extremely powerful and versatile method in mechanistic ion chemistry^{4–10}. Thus, a precursor ion is selected from the first mass spectrum and a daughter ion spectrum is obtained by collisionally activated dissociation (CAD) of this ion, using a collision gas (helium). We speculated that if a diazonium ion/crown 1:1 complex is only weakly held together in a cluster by van der Waals interactions, then the dissociation of the cluster should result in detection of the intact diazonium ion (ArN_2^{\oplus}) and the loss of the “neutral” crown. Will the charge remain only on the diazonium ion?

Results and Discussion

Partial FAB mass spectra and the corresponding CAD FAB MS-MS spectra are shown in Tables 1 and 2. The FAB mass spectrum of *o*-methylbenzenediazonium ion/18-crown-6 shows an abundant ArN_2^{\oplus} ion ($m/z = 119$), a diazonium ion/crown 1:1 complex ($m/z = 383$), and a two-cations-one-anion (tetrafluoroborate) cluster [$(\text{ArN}_2^{\oplus})_2\text{BF}_4^{\ominus}$; $m/z = 325$]. The ArN_2^{\oplus} /crown 1:1 complex ($m/z = 383$) was mass-selected and subjected to CAD analysis. The daughter ion spectrum shows the formation of abundant intact ArN_2^{\oplus} ($m/z = 119$) and its corresponding aryl cation ($m/z = 91$), indicative of N_2 loss upon collisional activation (impact dediazonation), in a 5:1 ratio. A low intensity cluster ion corresponding to

an aryl cation – crown 1:1 complex ($m/z = 355$) was also detected. In addition, ions corresponding to a (crown + H)[⊕] ($m/z = 265$) and [(crown – H)[⊕] or (crown + H – H₂)[⊕]] ($m/z = 263$) are observed. It is noteworthy that whereas both crown ions ($m/z = 265$ and 263) are present in the normal FAB spectrum (Figure 1), the relative abundance of the $m/z = 265$ ion is appreciably higher in the CAD spectrum (Figure 2). We attribute this observed differ-

Table 1. Partial FAB mass spectra [m/z (rel. abundance)] of $\text{ArN}_2^{\oplus}\text{BF}_4^{\ominus}$ /18-crown-6 complex

Substituent	FAB-MS ^{a)}		
<i>o</i> -Me	119	(42)	ArN_2^{\oplus}
	325	(15)	$(\text{ArN}_2^{\oplus})_2\text{BF}_4^{\ominus}$
	383	(8)	$\text{ArN}_2^{\oplus}(\text{crown})$
	647	(1)	$\text{ArN}_2^{\oplus}(\text{crown})_2$
<i>p</i> -NO ₂	150	(50)	ArN_2^{\oplus}
	414	(28)	$\text{ArN}_2^{\oplus}(\text{crown})$
	387	(15)	$(\text{ArN}_2^{\oplus})_2\text{BF}_4^{\ominus}$
<i>p</i> -Cl	139	(100)	ArN_2^{\oplus}
	141	(32)	ArN_2^{\oplus}
	403	(25)	$\text{ArN}_2^{\oplus}(\text{crown})$
	405	(7)	$\text{ArN}_2^{\oplus}(\text{crown})$
	365	(18)	$(\text{ArN}_2^{\oplus})_2\text{BF}_4^{\ominus}$
	367	(10)	$(\text{ArN}_2^{\oplus})_2\text{BF}_4^{\ominus}$
	667	(tiny)	$\text{ArN}_2^{\oplus}(\text{crown})$
669	(tiny)	$\text{ArN}_2^{\oplus}(\text{crown})$	
<i>p</i> -OMe	135	(51)	ArN_2^{\oplus}
	107	(18)	Ar^{\oplus}
	357	(12)	$(\text{ArN}_2^{\oplus})_2\text{BF}_4^{\ominus}$
	399	(6)	$\text{ArN}_2^{\oplus}(\text{crown})$

^{a)} Unless indicated otherwise, the base peaks were those of protonated 18-crown-6 or a crown fragment. In some cases a Na[⊕]/crown or a Cs[⊕]/crown was also observed.

ence to a possible contributing process involving proton transfer from acidic ArN_2^{\oplus} to basic crown oxygens, presumably by a benzyne mechanism¹⁷ (Scheme 1).

Table 2. FAB CAD/MS-MS spectra of $\text{ArN}_2^{\oplus}\text{BF}_4^{\ominus}$ /18-crown-6 complex

Substituent	Mass-selected m/z (base peak intensity)	Products [m/z (rel. abundance)] ^{a)}	
<i>o</i> -Me	383 ArN_2^{\oplus} (crown) (17.96)	119 (80)	ArN_2^{\oplus}
		91 (16)	Ar^{\oplus}
		355 (5)	Ar^{\oplus} (crown)
		265 (19)	(crown + H) [⊕]
<i>p</i> -NO ₂	414 ArN_2^{\oplus} (crown) (9.47)	150 (30)	ArN_2^{\oplus}
		122 (9)	Ar^{\oplus}
<i>p</i> -NO ₂	387 (ArN_2^{\oplus}) ₂ BF_4^{\ominus} (0.82)	263 (9)	(crown - H) [⊕]
		150 (60)	ArN_2^{\oplus}
		122 (12)	Ar^{\oplus}
		139 (80)	(ArN_2^{\oplus})
<i>p</i> -Cl	403 ArN_2^{\oplus} (crown) (1.05)	141 (24)	(ArN_2^{\oplus})
		111 (20)	(Ar^{\oplus})
		113 (9)	(Ar^{\oplus})
		375 (14)	Ar^{\oplus} (crown)
		377 (4)	Ar^{\oplus} (crown)
		263 (5)	(crown - H) [⊕]
<i>p</i> -OMe	399 ArN_2^{\oplus} (crown) (0.71)	135 (35)	(ArN_2^{\oplus})
		107 (3)	(Ar^{\oplus})
		263 (3)	(crown - H) [⊕]

^{a)} 10-fold sensitivity enhancement applied.

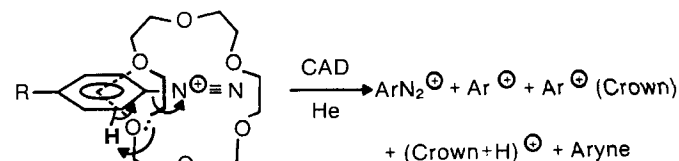
The FAB mass spectrum of *p*-nitrobenzenediazonium/18-crown-6 exhibits an intact ArN_2^{\oplus} ($m/z = 150$), a diazonium ion-crown ether 1:1 complex ($m/z = 414$), and a two-cations-one-anion cluster [(ArN_2^{\oplus})₂ BF_4^{\ominus} ; $m/z = 387$].

The MS-MS experiment was performed on both $m/z = 414$ and $m/z = 387$ ions. The former dissociates on collision to produce ArN_2^{\oplus} ($m/z = 150$) and Ar^{\oplus} ($m/z = 122$) in a 3.3:1 ratio.

We note here that in the CAD mass spectrum, the relative abundance of $m/z = 263$ ion (crown - H)[⊕] has increased substantially

relative to $m/z = 265$ ($263/265 = 6$ versus $263/265 = 0.82$). A CAD experiment on (ArN_2^{\oplus})₂ BF_4^{\ominus} cluster resulted in dissociation to ArN_2^{\oplus} and Ar^{\oplus} in a 5:1 ratio.

Scheme 1. Collisionally activated dissociation of a 1:1 complex [heterolytic dediazonium and crown protonation via an aryne]



With *p*-chlorobenzenediazonium ion/18-crown-6 system, the FAB spectrum exhibits abundant ArN_2^{\oplus} ($m/z = 139, 141$) in addition to an ArN_2^{\oplus} /crown 1:1 complex ($m/z = 403, 405$), a two-cations-one-anion cluster ($m/z = 365, 367$) and a tiny ArN_2^{\oplus} /crown 1:2 cluster. Collisional dissociation of the ArN_2^{\oplus} /crown 1:1 cluster ($m/z = 403$) results in detection of abundant ArN_2^{\oplus} ions ($m/z = 139, 141$), as well as Ar^{\oplus} (111, 113). Complexation of Ar^{\oplus} to the crown results in the detection of a small 1:1 cluster ion ($m/z = 375, 377$). We observe a drastic increase in the abundance of the (crown - H)[⊕] ion relative to (crown + H)[⊕] in the CAD/MS-MS spectrum.

With *p*-methoxybenzenediazonium ion, the normal FAB spectrum exhibits the intact ArN_2^{\oplus} ($m/z = 135$), the Ar^{\oplus} ($m/z = 107$) and a two-cations-one-anion cluster [(ArN_2^{\oplus})₂ BF_4^{\ominus} ; $m/z = 357$], in addition to the ArN_2^{\oplus} /crown 1:1 complex ($m/z = 399$). The latter ion dissociates on collision with He to give the intact ArN_2^{\oplus} ($m/z = 135$) and its corresponding aryl cation ($m/z = 107$) in a 5:1 ratio, in addition to a (crown - H)[⊕] ion ($m/z = 263$).

We propose two mechanisms which could contribute to the formation of the $m/z = 263$ ion:

a) The aryl cation formed upon collisional dediazonium abstracts a hydride ion from the crown host molecule within the 1:1 cluster to form (crown - H)[⊕] and ArH (Scheme 2).

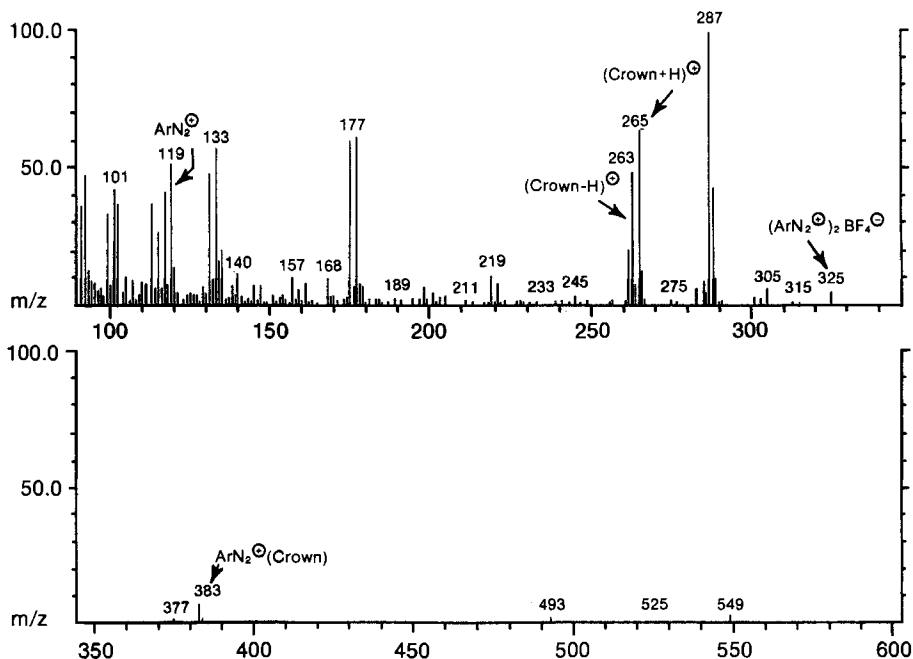


Figure 1. FAB mass spectrum of *o*-MePhN₂[⊕]BF₄[⊖]/18-crown-6

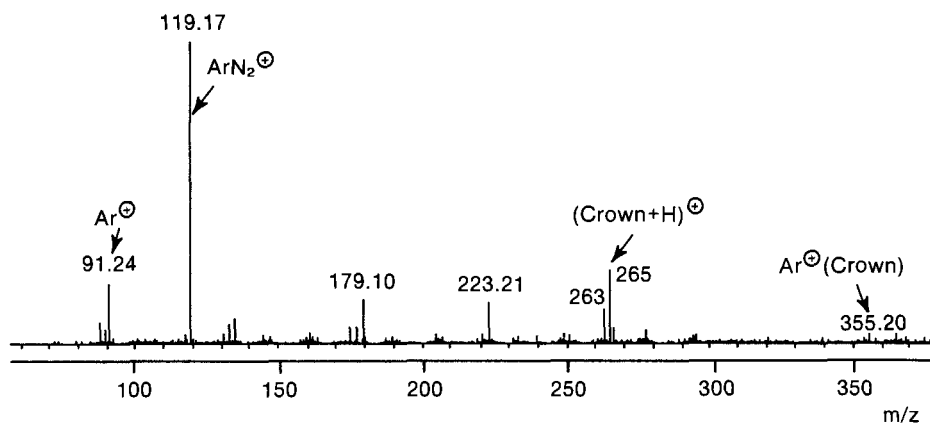
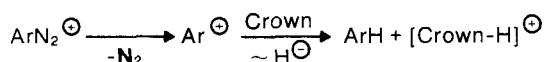


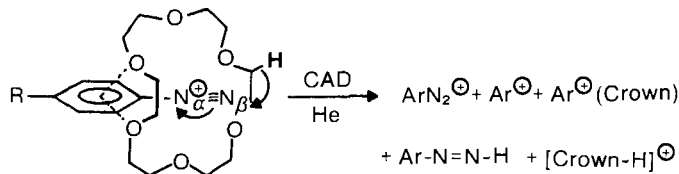
Figure 2. FAB CAD/MS-MS spectrum of $m/z = 383$ ion $[\text{ArN}_2^+(\text{crown}) (1:1)]$

Scheme 2. Collisionally induced heterolytic dediazonation and hydride abstraction from crown by Ar^\oplus



b) Alternatively, the acidic N_β could abstract a hydride from the crown to form $(\text{crown} - \text{H})^\oplus$ and an aryldiimide $\text{Ar}-\text{N}=\text{NH}$ (Scheme 3), a mechanism which is somewhat similar to $\text{ArN}=\text{NH}$ formation via ArN_2^+ and $\text{CH}_3\text{O}^\ominus$ in the condensed phase where $\text{CH}_3\text{O}^\ominus$ is the hydride source¹⁷.

Scheme 3. Collisionally activated dissociation of a 1:1 complex [hydride abstraction by N_β and formation of a $(\text{crown} - \text{H})^\oplus$ ion]



The presence of electron-withdrawing substituents enhances the positive charge the diazonio group. This should increase crown complexation as well as the possibility of hydride abstraction (a more electron-deficient N_β). On the other hand, electron-donating substituents increase the diazo character through mesomeric and/or inductive effects. This should weaken crown complexation and also reduce the possibility of hydride abstraction. Whereas this argument seems to fit in well with our observations with the *p*-nitro- and *p*-chlorobenzenediazonium ions, an ionic hydride transfer mechanism for *p*-methoxybenzenediazonium ion, for which the diazo character is expected to be important, is less favorable, and a hydride transfer mechanism involving Ar^\oplus appears more satisfactory.

Studies with deuterium-labeled diazonium ions and crowns and guest–host complexation involving carbocations, carbodocations, and Meerwein salts with suitably functionalized calixarenes and cyclodextrins are in progress.

I am grateful to Professor H. Zollinger (ETH, Zürich) for his interest in our work and encouragement. Professors J. Allison (Michigan State) and C. Wesdemiotis (University of Akron) and Dr. R. P. Lattimer (BF Goodrich) are thanked for valuable discussions. My special thanks to Dr. D. Gage (Center for MS, MSU) for recording the MS-MS spectra.

Experimental

Sample preparation and introduction into the mass spectrometer was as already described^{1,3}.

The FAB mass spectral data were acquired by use of a Finnigan MAT 311 A/INCOS 2400 mass spectrometer system equipped with an EI/FD/FAB ion source. High-energy xenon (8 kV) was used to effect sputtering. The FAB CAD MS-MS experiments were performed on a JEOL HX 110 HF double-focussing mass spectrometer at the NIH Center for Mass Spectrometry at Michigan State University. Linked scans were used at constant B/E . Helium was used as collision gas in a cell located in the first field-free region. The helium pressure was adjusted to reduce the abundance of the parent ion by 50%. A JEOL DA-5000 data system generated the linked scans.

CAS Registry Numbers

18-crown-6/*o*-methylbenzenediazonium tetrafluoroborate complex: 126541-37-5 / 18-crown-6/*p*-nitrobenzenediazonium tetrafluoroborate complex: 74317-27-4 / 18-crown-6/*p*-chlorobenzenediazonium tetrafluoroborate complex: 74317-29-6 / 18-crown-6/*p*-methoxybenzenediazonium tetrafluoroborate complex: 74317-32-1

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