Site of Protonation of Benzonitrile

Hydrogen Interchange in the Protonated Species

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The site of protonation of gaseous benzonitrile in reactions with H_3^+ , CH_3OH_2^+ , and CH_3CNH^+ as protonating agents has been examined by using tandem mass spectrometry in combination with deuterium and ^{13}C labeling. Metastable and collision-induced dissociation studies of $\text{C}_6\text{X}_5\text{CNX}^+$ ($\text{X} = \text{H}$ or D) show that proton attachment occurs on the CN group. The metastably decomposing $\text{C}_6\text{X}_5\text{CNX}^+$ leads only to $\text{C}_6\text{X}_5^+ + \text{XCN}$. This reaction proceeds via a mechanism involving H^+ (D^+) transfer from the CN group to the phenyl ring in which H/D exchange occurs. The efficiency of the CN-to-ring H^+ (D^+) transfer increases in the order para < meta < ortho position. Evidence for incomplete H/D atom randomization in $\text{C}_6\text{X}_5\text{CNX}^+$ prior to XCN loss has been obtained. Both processes, CN-to-ring H/D exchange and H/D exchange at the phenyl ring, are affected by the internal energy of the $\text{C}_6\text{X}_5\text{CNX}^+$ ions. The results have been interpreted in terms of the internal energy distribution of the ions fragmenting within the metastable time window. Collision-induced dissociation of $\text{C}_6\text{X}_5\text{CNX}^+$ causes the energy-enriched ions to decompose by direct bond cleavage into $\text{C}_6\text{X}_5^+ + \text{XCN}$. (*J Am Soc Mass Spectrom* 1990, 1, 225-232)

Intermolecular proton transfer and intramolecular hydrogen or proton migrations are of considerable importance for the elucidation of mechanistic details of organic reactions. It is therefore not surprising that these processes have been the subject of many investigations [1] in the field of gas-phase ion chemistry.

This paper reports a detailed study of the initial site of protonation of benzonitrile and the unimolecular chemistry of the protonated (deuterated) species. Our interest in this problem was stimulated by a controversy in the literature [2-4] regarding the site of protonation. In the study of H/D exchange reactions of protonated aromatic compounds with D_2O by ion cyclotron resonance spectroscopy, Beauchamp and co-workers [2] noted that with sufficiently acidic donors, for example, D_3O^+ , protonation of benzonitrile occurs on both the ring and the substituent. Lau and Kebabian [3] argued on the basis of proton transfer equilibrium measurements that the CN group is protonated. On the other hand, more recently Meot-Ner and co-workers [4] stated that ring protonation is energetically favored over CN protonation.

To obtain direct experimental evidence on proton exchange reactions in protonated benzonitrile, we studied its metastable ion (MI) and collision-induced dissociations (CID) by mass-analyzed ion kinetic en-

ergy (MIKE) spectroscopy in combination with deuterium and ^{13}C labeling experiments. To provide additional information concerning the reaction mechanism, these species were produced in reactions of different protonation exothermicity under chemical ionization (CI) conditions.

Experimental

All experiments were carried out with a VG ZAB-2HF mass spectrometer that was coupled to a VG 11/250 data system (VG Analytical Ltd., Manchester, UK) using the CI source and techniques identical to those applied in our previous studies [5, 6]. Only a brief description of the experimental conditions will be given here.

The ion source was operated under the following conditions: accelerating voltage, 8 kV; ionizing electron energy, 70 eV; ion repeller potential with respect to the source chamber, 0 V; ion source temperature, $\sim 180^\circ\text{C}$. The protonated benzonitrile ions, $(\text{C}_6\text{X}_5\text{CN})\text{X}^+$ (where $\text{X} = \text{H}$ and D), were generated by CI of benzonitrile 1 and the analogues labeled with ^{13}C and deuterium, 1a-1e (Scheme 1), using H_2 , D_2 , CH_3OH , CD_3OD , and CD_3CN as reagent gases. The typical concentration of benzonitrile inside the source was $\sim 3 \times 10^{12}$ molecules/ cm^3 , that is, $\sim 1 \times 10^{-4}$ mbar, as estimated [5] from the reading of the ionization gauge

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Scheme I

at the entrance to the diffusion pump ($P_i = 2 \times 10^{-7}$ mbar); the total source pressure was sufficient to give an ionization gauge reading of $\sim 10^{-6}$ mbar.

Under these conditions, peaks due to ions with a relative abundance $\geq 10\%$ are observed at m/z 19 (23%), m/z 103 (60%), and m/z 104 (100%) in the spectrum of the H_2 - $\text{C}_6\text{H}_5\text{CN}$ mixture; at m/z 15 (16%), m/z 29 (18%), m/z 31 (31%), m/z 32 (13%), m/z 33 (100%), m/z 103 (50%), and m/z 104 (50%) in the spectrum of the CH_3OH - $\text{C}_6\text{H}_5\text{CN}$ mixture; and at m/z 42 (62%), m/z 44 (86%), m/z 46 (100%), m/z 103 (43%), and m/z 105 (19%) in the spectrum of the CD_3CN - $\text{C}_6\text{H}_5\text{CN}$ mixture. The production of the protonated benzonitrile species therefore may be attributed mainly to the following reactions:

The MIKE spectra of the metastable ions were studied by selecting and focusing the $(\text{C}_6\text{X}_5\text{CN})\text{X}^+$ species into the second field-free region (2 FFR), that is, between the magnetic (B) and electric (E) analyzers, and scanning the voltage of E. CID/MIKE spectra were obtained by introducing He as target gas into the collision cell located in 2 FFR. The He pressure in the cell was varied over the range 3.5×10^{-5} to 3.7×10^{-4} mbar, as estimated [7] from the ionization gauge reading situated in this region.

Table 1. MIKE spectra of the $\text{C}_6\text{X}_5\text{CNH}^+$ metastable ions generated from various sources

Initial ion	Source		m/z of daughter ions ^a			
	System	Reaction	77	78	79	α' ^b
	H_2 -1	1	100			
	H_2 -1a	1	100			
	H_2 -1b	1	45	55		0.45
	CH_3OH -1b	2	34	66		0.34
	H_2 -1c	1	16	84		0.16
	CH_3OH -1c	2	30	70		0.30
	H_2 -1d	1	8	92		0.08
	CH_3OH -1d	2	24	76		0.24
	H_2 -1e	1		20	80	0.20
	CH_3OH -1e	2		29	71	0.29

^a Abundances are expressed as percentages of the sum.

^b Fraction of D transferred from the phenyl ring to the nitrile group, expressed as the ratio $\alpha' = \text{C}_6\text{H}_{5-n}\text{D}_{n-1}^+(\text{C}_6\text{H}_{5-n}\text{D}_{n-1})^+ / (\text{C}_6\text{H}_{5-n}\text{D}_{n-1}^+ + \text{C}_6\text{H}_5\text{D}_n^+)$.

Table 2. MIKE spectra of the $C_6X_5CND^+$ metastable ions generated from various sources

Initial ion	Source		<i>m/z</i> of daughter ions ^a				α^b
	System	Reaction	77	78	79	80
2'	D ₂ -1	1	51	49			0.49
	CD ₃ OD-1	2	66	34			0.34
	CD ₃ CN-1	3	100				0
2a'	D ₂ -1a	1	51	49			0.49
2b'	D ₂ -1b	1		63	37		0.37
2c'	D ₂ -1c	1		60	40		0.40
2d'	D ₂ -1d	1		61	39		0.39
2e'	D ₂ -1e	1			69	31	0.31

^a Abundances are expressed as percentages of the sum.^b Fraction of D transferred from the nitrile group to the phenyl ring expressed as the ratio $\alpha = C_6H_5-nD_n^+ / (C_6H_5-nD_n^+ + C_6H_5-nD_{n-1}^+)$.

Materials

Helium, H₂, and D₂ (Matheson), CH₃OH (Aldrich), and CD₃OD, CD₃CN, and C₆H₅CN (Merck) were obtained commercially and were used without further purification. Carbon-13-labeled benzonitrile **1a** was available from a previous study [8]. The D-labeled benzonitriles **1b-1e** were obtained by dehydration [9] of the corresponding benzamides, which were available from an earlier study [10]. All labeled compounds **1a-1e** were purified by GC using a silicone OV 1 column at 150 °C.

Results and Discussion

The MI/MIKE spectrum of the protonated benzonitrile species **2** generated by reaction 1 shows (Table 1) only one ionic fragment observed at *m/z* 77 (C₆H₅⁺), which arises from the metastable ion dissociation reaction

The MI spectra of the labeled ions (C₆H₅CN)D⁺ (**2'**) and (C₆H₅¹³CN)H⁺ (**2a**) prepared from CD₃CN-1 (re-

action 3) and H₂-1a (reaction 1), respectively, show (Tables 1 and 2) that both D and ¹³C are specifically eliminated in the (C, X, N). These results indicate that H⁺ in (C₆H₅CN)H⁺ is attached to the CN group rather than to the phenyl ring.

As can be seen in Table 2, in the case of ions **2'** generated from the D₂-1 (reaction 1) and CD₃OD-1 (reaction 2) systems, the formation of C₆H₄D⁺ (*m/z* 78) is observed in addition to that of C₆H₅⁺ (*m/z* 77).

Taking into account that CID experiments on the stable ions **2'** strongly support that they have been formed in reactions 1-3 by D⁺ attachment to the CN group only (see below), it follows that before fragmentation (reaction 4) the CN-to-ring H/D exchange occurs in the C₆H₅CND⁺ species generated by reactions 1 and 2. The thermochemical data (Table 3) predict that reactions 1 and 2 are more exothermic than reaction 3.

The observed fractions of D transferred from the CN group to the phenyl ring, expressed as the ratio

$$\alpha = C_6H_5-nD_n^+ / (C_6H_5-nD_n^+ + C_6H_5-nD_{n-1}^+)$$

are different for ions **2'** generated from D₂-1 and CD₃OD-1 (Table 2). This can be attributed to the differ-

Table 3. Heats of formation used in this work

Species	ΔH_{f298}^0 (kcal/mol)	Species	ΔH_{f298}^0 (kcal/mol)
CN	104.0	H ₃ ⁺	264.5
HCN	32.3	CN ⁺	428.9
HNC	48 ± 2	HCN ⁺	346
CH ₃ CN	18	HNC ⁺	336
CH ₃ OH	-48.2	CH ₃ CNH ⁺	195
C ₆ H ₅	79 ± 1	CH ₃ OH ₂ ⁺	136
C ₆ H ₆	119.8	C ₆ H ₆ ⁺	269.3
C ₆ H ₅ CN	52	C ₆ H ₆ ⁺	233.2
		C ₆ H ₅ CNH ⁺	222

Source: All values taken from ref. 20.

ences in the excess energy of **2'** formed in reactions 1 and 2. Moreover, these results reflect that the product-determining step of the CN-to-ring H⁺ (D⁺) transfer is controlled more by the energy barrier than by the frequency factor. The magnitude of this barrier is probably relatively low (below 14 kcal/mol), as can be inferred from the observed α values for ions **2'** together with the protonation exothermicities of reactions 1-3. The data in Table 4 clearly show that the H/D atoms in C₆H₅CND⁺ derived from reaction 1 are not statistically equilibrated before loss of (C, X, N). Complete statistical scrambling of H/D in **2'** would lead to the ratio C₆H₄D⁺/C₆H₅⁺ of 5, whereas the ratio found for both **2'** and **2a'** is 0.96, which corresponds to a value of 1, assuming complete equilibration of D at the CN group and one H atom at the phenyl ring. The results obtained for other ions listed in Table 3 are quite similar to those obtained for **2'** and **2a'**.

All these observations imply that the H (D) atoms from an ortho position of the phenyl ring in the CN-to-ring H/D exchange are mainly involved. To obtain

additional information about the H/D exchange between the CN group and the phenyl ring, the extent of D transfer from the ortho, meta, and para positions to the CN group has been examined using the site-specifically deuterated analogues **2b-2e** (Table I).

As the MI spectra in Figures 1a-1e and Table 1 show, the fraction of D transferred from the ring positions to the CN group, expressed as

$$\alpha' = \frac{C_6H_{6-n}D_{n-1}^+}{C_6H_{6-n}D_{n-1}^+ + C_6H_{5-n}D_n^+}$$

decreases in the order ortho>meta>para for the ions generated by both reactions 1 and 2.

The large differences in the α' values found for ions **2b-2d** derived from reaction 1 reveal that H/D exchange in the phenyl ring is far from equilibrium prior to unimolecular dissociation. A relatively high value of α' observed for ions **2b** generated from H₂-**1b**, as compared to ions **2c** and **2d** (Table 1), strongly supports the conclusion on the favored ortho position in the CN-to-ring exchange. A mechanism involving the latter process in ions **2b** is proposed in Scheme II.

In nitrogen-protonated benzonitrile, the charge can be delocalized via a resonance structure at the cyano carbon atom, so that the cyano group is likely to be no longer linear, thus permitting first a proton transfer from the cyano group to the ortho ring position **2b** → **3b**, which then may be followed by a 1,2 H or D shift to the ipso position to give intermediate **4b**. From this intermediate, XCN can be eliminated via a 1,1 elimination, which is also a thermochemically favored process (Figure 2).

The H⁺ transfer from the CN group to the ipso position and vice versa via the bridged form intermediate **3b'**, as shown in Scheme III, is expected to be a high energy demanding process.

Table 4. The H/D exchange between the CN group and the phenyl ring in the C₆H₅CN⁺ metastable ions generated from X₂/C₆H₅CN

Species	Ratios					
	C ₆ H ₄ D ⁺ /C ₆ H ₅ ⁺		C ₆ H ₃ D ₂ ⁺ /C ₆ H ₄ D ⁺		C ₆ H ₂ D ₃ ⁺ /C ₆ H ₃ D ₂ ⁺	
	Obs.	Stat.	Obs.	Stat.	Obs.	Stat.
2'	0.96	1 ^a ; 2 ^b ; 5 ^c				
2a'	0.96	1 ^a ; 2 ^b ; 5 ^c				
2b'			0.59	0.33 ^a ; 0.5 ^b ; 2 ^c		
2c'			0.67	1 ^a ; 2 ^b ; 2 ^c		
2d'			0.64	1 ^a ; 2 ^b ; 2 ^c		
2e'					0.45	1 ^a ; 2 ^b ; 1 ^c
2b	1.22	3.0 ^a ; 2 ^b ; 5 ^c				

Statistical values were obtained assuming randomization between:

^a X atom at the CN group and one X atom at the ortho position of the phenyl ring.

^b X atom at the CN group and two X atoms at the ortho ring positions.

^c X atom at the CN group and the five X atoms at the phenyl ring.

Figure 1. Metastable dissociation spectra of $C_6H_4DCNH^+$ generated from the systems (a) $H_3^+(H_2)-1b$, (b) $H_3^+(H_2)-1c$, (c) $H_3^+(H_2)-1d$, (d) $CH_3OH_2^+(CH_3OH)-1c$, and (e) $CH_3OH_2^+(CH_3OH)-1d$. The background pressure was 2×10^{-9} mbar.

Figure 2. Thermochemical thresholds for the dissociation channels of $C_6H_5CNH^+$ obtained from the heats of formation given in Table 2.

On the basis of the calculated barrier for conversion of HNC^{++} into HCN^{++} via a transition state resembling a complex of H^+ and CN^- [11], the critical energy for the route $2b \rightarrow 3b' \rightarrow 4b'$ should probably be in the range of 45–75 kcal/mol. Because our experiments imply a much lower value (<14 kcal/mol) for the CN-to-ring H/D exchange barrier, it may be concluded that the mechanism shown in Scheme III is not operative.

Obviously, in the cases of ions $2c-2e$, the H^+ transfer through space from the CN group to the deuterated meta and para positions is expected to be less probable than transfer to the deuterated ortho position in $2b$, if it occurs at all, because of the large dis-

tances to be overcome. It is more likely that in the ions $2c-2e$ the CN-to-ring H/D exchange proceeds by a pathway similar to that illustrated in Scheme II for ions $2b$. After H^+ transfer from the CN group to the ortho ring position, the H/D exchange may occur via 1,2 H/D shifts along the phenyl ring until eventually the intermediate $4b$ is formed from which XCN can be lost. Although the energy barrier for proton migration along the aromatic ring of ions 2 is not known, it is probably relatively low, judging by the reported activation energy of 10 kcal/mol for hydrogen scrambling in protonated benzene [12], the theoretically predicted [13] barrier of 7.7 kcal/mol between the π and σ complexes of this species and the estimated [14] barriers of $\sim 3-25$ kcal/mol for the proton transfer between different ring positions in alkyl-substituted benzenium ions. One might expect, therefore, that the activation barrier for H/D exchange along the phenyl ring of ions $2b-2e$ is low enough (compared to that related to the loss of HCN, Figure 2) to reach a complete randomization prior to elimination of XCN. However, the fact that the observed α' values depend on the initial position of the D atom in the phenyl ring (Table 1) indicates that this is not the case and suggests that the product-determining step of the CN-to-ring H/D exchange in ions $2c-2e$ is associated with H (D) migration along the phenyl ring. Moreover, these observations imply that the rate of this process is comparable to that of MI fragmentation (reaction 4), corroborating the reported slow H/D exchange at the aromatic ring in metastably decomposing (3-phenyl-2-propynyl) benzenium ions and in protonated benzaldehydes and acetophenones [15] and being different from the reported [14, 16] complete H/D exchange in the aromatic ring of benzenium ions prior to fragmentation.

The incomplete H/D exchange at the aromatic ring of ions $2b-2e$ versus the complete hydrogen scrambling in protonated benzene [16a] suggests that the cyano group has a significant influence on the rate of hydrogen migration along the phenyl ring.

STO-3G calculations [17] predict that the CN group destabilizes the cyclohexadienyl cation regardless of the site of substitution. Therefore, H^+ (D^+) migration from the ring positions of the $3b$ -type intermediates toward the CN group—being a strong electron-withdrawing substituent and acting as π base—rather than along the ring positions can be expected. This may lead to the limited H/D exchange at the phenyl ring seen in ions $2b-2e$.

Scheme III

Figure 3. Schematic representation of the internal energy distribution for ions generated from reaction 1 ($\text{H}_3^+ + \text{C}_6\text{H}_5\text{CN} \rightarrow \text{C}_6\text{H}_5\text{CNH}^+ + \text{H}_2$) and reaction 2 ($\text{CH}_3\text{OH}_2^+ + \text{C}_6\text{H}_5\text{CN} \rightarrow \text{C}_6\text{H}_5\text{CNH}^+ + \text{CH}_3\text{OH}$).

Interestingly, while the α' and α values for ions **2b** and **2'**, respectively, are greater if they have been generated via reaction 1 rather than via reaction 2, the reverse is true for ions **2c-2e** (Tables 1 and 2). This effect may be interpreted in terms of a competition between H/D exchange and elimination of XCN. If the rates of H^+ (D^+) transfer from the CN group to the phenyl ring ($2 \rightarrow 3\text{b}$) and H/D exchange within intermediate **3b** relative to fragmentation in the metastable

time window are markedly dependent on the internal energy, then ions generated by different CI reactions and having different internal energy distributions in this time window may lead to differences in the extent of CN-to-ring H/D exchange.

Taking into account the exothermicities of reactions 1 and 2, it is reasonable to expect that the internal energy distribution of metastable ions arising from reaction 1 would be shifted to higher energy compared to those from reaction 2, as illustrated in Figure 3.

In the case of ions **2c-2e**, the CN-to-ring H/D exchange efficiency will depend mainly on the relative rates of H/D exchange at the phenyl ring versus dissociation by loss of XCN. Since the barrier for H/D exchange is much lower than the threshold for elimination of XCN, the internal energy increase will greatly favor dissociation according to RRKM theory [18]. Thus, relative to dissociation, the rate of exchange will decrease with increasing internal energy of the reacting ions, giving the lower α' values for the CN-to-ring H/D exchange. This is precisely the behavior exhibited by ions **2c-2e** derived from reactions 1 and 2 (Table 1). However, the situation is somewhat different for ions **2'** and **2b**, where, as mentioned above, the extent of CN-to-ring exchange found for ions derived from reaction 1 is higher than for those from reaction 2 (Ta-

Figure 4. (a) The ion current ratios $\alpha = \text{C}_6\text{H}_4\text{D}^+ / (\text{C}_6\text{H}_4\text{D}^+ + \text{C}_6\text{H}_5^+)$ for $\text{C}_6\text{H}_5\text{CND}^+$ generated from $\text{D}_3^+(\text{D}_2) - \text{C}_6\text{H}_5\text{CN}$ ($\circ$); $\text{CD}_3\text{OD}_2^+(\text{CD}_3\text{OD}) - \text{C}_6\text{H}_5\text{CN}$ ($\bullet$) and $\text{CD}_3\text{CND}^+(\text{CD}_3\text{CN}) - \text{C}_6\text{H}_5\text{CN}$ (Δ) as a function of the collision gas (He) pressure. (b) The ion current ratios $\alpha' = \text{C}_6\text{H}_5^+ / (\text{C}_6\text{H}_5^+ + \text{C}_6\text{H}_4\text{D}^+)$ for the $\text{C}_6\text{H}_4\text{-DCNH}^+$ ions indicated (generated from $\text{H}_3^+(\text{H}_2) - \text{C}_6\text{H}_4\text{DCN}$) as a function of the collision gas (He) pressure. The values at $P(\text{He}) = 2 \times 10^{-9}$ mbar correspond to background pressure.

bles 1 and 2). This can be understood if the H/D exchange between the CN group and the ortho ring position is controlled predominantly by the energy barrier associated with the H^+ (D^+) transfer process, $2 \rightarrow 3b$ (Scheme II), which at lower protonation exothermicities can no longer compete effectively with dissociation of the $(C_6H_5CN)H^+$ ions via reaction 4.

It should be added that the results of the present work support the earlier observations [19] indicating the influence of the internal energy distribution on metastable ion decompositions in 2 FFR.

Further information on the hydrogen migration in the protonated benzonitrile species has been obtained from the CID/MIKE spectra. As can be derived from Figure 4a, upon CID, ion $2'$ prepared from $CD_3CN-C_6H_5CN$ undergoes, in contrast to spontaneous dissociation, CN-to-ring H/D exchange as manifested by the observed ratio $\alpha = C_6H_4D^+ / (C_6H_4D^+ + C_6H_5^+)$ as a function of the target gas pressure, $P(He)$. The behavior of α with $P(He)$ displayed in Figure 4a reflects the fact that as the internal energy of the reacting ions generated by reactions 1 and 2 is increased by increasing the number of collisions (by increasing the collision gas pressure), the formation of $C_6H_4D^+$ becomes less competitive with respect to that of $C_6H_5^+$. These observations together with the α values found for metastably decomposing ions $2'$ generated from reactions 1-3 (Table 2) suggest that highly excited (by collisional activation) protonated benzonitrile species undergo a direct dissociation by HNC loss. The thermochemical threshold for $C_6H_5^+ + HNC$ formation is higher in energy than that for $C_6H_5^+ + HCN$ formation (Figure 2). Therefore, it may well be that ions having a relatively high internal energy react via the direct and entropically favored process $2 \rightarrow C_6H_5^+ + HNC$. From Figure 4 it follows that the probability of this process increases as the internal energy of the reacting ions increases. In addition, these experiments support the conclusion that proton attachment in the reactions of benzonitrile with the protonating agents such as H_3^+ , $CH_3OH_2^+$, and CH_3CNH^+ occurs at the CN group.

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References

- (a) Benoit, F. M.; Harrison, A. G. *Org. Mass Spectrom.* **1976**, *11*, 599, 1056. (b) Benoit, F. M.; Harrison, A. G.; Lossing, F.

- P. Org. Mass Spectrom.* **1977**, *12*, 78. (c) Leung, H. W.; Harrison, A. G. *Org. Mass Spectrom.* **1977**, *12*, 582. (d) Benoit, F. M.; Harrison, A. G. *J. Am. Chem. Soc.* **1977**, *99*, 3980. (e) Kuck, D.; Bther, W.; Grtzmacher, H.-F. *J. Am. Chem. Soc.* **1979**, *101*, 7154. (f) Kuck, D.; Grtzmacher, H.-F. *Z. Naturforsch.* **1979**, *34b*, 1750. (g) Zwinseleman, J. J.; Nibbering, N. M. M.; Ciommer, B.; Schwarz, H. In *Tandem Mass Spectrometry*; F. W. McLafferty, Ed.; Wiley: New York, 1983; chapter 4. (h) Groenewold, G. S.; Gross, M. L. In *Ionic Processes in the Gas Phase*; Almoester Ferreira, M. A., Ed.; D. Reidel: Dordrecht, 1984; pp 243-265. (i) Fornarini, S.; Speranza, M. *J. Am. Chem. Soc.* **1985**, *107*, 5358. (j) Bther, W.; Kuck, D.; Grtzmacher, H.-F. *Org. Mass Spectrom.* **1985**, *20*, 589. (k) Schwarz, H. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; chapter 4. (l) Harrison, A. G. *Org. Mass Spectrom.* **1987**, *22*, 637. (m) Grtzmacher, H.-F.; Thielking, G. *Org. Mass Spectrom.* **1988**, *23*, 397.
- Freiser, B. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 6893.
- Lau, Y. K.; Kebabian, P. *J. Am. Chem. Soc.* **1976**, *98*, 7452.
- Meot-Ner (Mautner), M.; Karpas, Z.; Deakyne, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 3913.
- Wincel, H.; Fokkens, R. H.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Processes* **1989**, *88*, 241.
- Wincel, H.; Fokkens, R. H.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Processes* **1989**, *91*, 339.
- Lange, W. de.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Processes* **1988**, *86*, 287.
- Molenaar-Langeveld, T. A.; Fokkens, R. H.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1986**, *21*, 15.
- Campagna, F.; Cavotti, A.; Casini, G. *Tetrahedron Lett.* **1977**, 1813.
- Bruins, A. P.; Nibbering, N. M. M.; Boer, T. J. de *Tetrahedron Lett.* **1972**, 1109.
- Koch, W.; Frenking, G.; Schwarz, H. *Naturwissenschaften* **1984**, *71*, 473.
- Olah, G. A.; Schlosberg, R. H.; Kelly, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 2546.
- Sordo, T.; Bertran, J.; Canadell, E. *J. Chem. Soc., Perkin Trans.* **1979**, *2*, 1486.
- Bther, W.; Grtzmacher, H.-F. *Int. J. Mass Spectrom. Ion Processes* **1985**, *64*, 193.
- (a) Bther, W.; Kuck, D.; Grtzmacher, H.-F. *Org. Mass Spectrom.* **1985**, *20*, 572. (b) Filges, U.; Grtzmacher, H.-F. *Org. Mass Spectrom.* **1986**, *21*, 673; **1987**, *22*, 444.
- (a) Bruins, A. P.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1976**, *11*, 950. (b) Kuck, D.; Bther, W. *Org. Mass Spectrom.* **1986**, *21*, 451.
- (a) McElvey, J. M.; Alexandratos, S.; Streitwieser, A., Jr.; Abboud, J. L. M.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 244. (b) Paddon-Row, M. N.; Santiago, C.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6561.
- Forst, W. *Theory of Unimolecular Reactions*; Academic: New York, 1973.
- (a) Harrison, A. G.; Gumann, T.; Stahl, D. *Org. Mass Spectrom.* **1983**, *18*, 517. (b) Reiner, E. J.; Poirier, R. A.; Peterson, M. P.; Csizmadia, I. G.; Harrison, A. G. *Can. J. Chem.* **1986**, *64*, 1652.
- Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data Suppl.* **1988**, *17*.