Ion-Neutral Complexes in Gas-Phase Dissociations of Protonated Nitriles: $n\text{-C}_3\text{H}_7\text{CNH}^+$ and $i\text{-C}_3\text{H}_7\text{CNH}^+$

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In the last decade ion-neutral complexes have been proposed frequently as intermediates in the unimolecular dissociation of many organic ions in the gas phase [1]. For example, for the unimolecularly fragmenting ions $n\text{-C}_3\text{H}_7\text{R}^+$ and $i\text{-C}_3\text{H}_7\text{R}^+$, where a.o. $\text{R} = \text{CH}_2\text{O}$, CH_3CHO and $(\text{CH}_3)_2\text{CO}$ [2], $\text{CH}_2 = \text{NH}$ [3a] and $\text{CH}_3\text{CH} = \text{NH}$ [3b] and CO [4], ion-neutral complexes have been invoked to rationalize the intramolecular isomerization of $[n\text{-C}_3\text{H}_7 \dots \text{R}]$ into $[i\text{-C}_3\text{H}_7 \dots \text{R}]$ before elimination of R or, in appropriate systems, the derived alkene(R-H) [2–4]. However, for $\text{R} = \text{CO}$ the presumed involvement of such complexes is very difficult to verify experimentally, as in that case a possible interaction between the C_3H_7^+ and CO species prior to their separation cannot be probed by H/D exchange.

We report here on the occurrence of ion-neutral complexes in the unimolecular fragmentation of the metastable ions $n\text{-C}_3\text{H}_7\text{CNH}^+$, **1**, and $i\text{-C}_3\text{H}_7\text{CNH}^+$, **2**, which are iso-electronic with $n\text{-C}_3\text{H}_7\text{CO}^+$ and $i\text{-C}_3\text{H}_7\text{CO}^+$, respectively. The proton (deuteron) on nitrogen in these ions serves as a valuable tool to probe the interaction between the C_3H_7^+ ion and the (H,C,N) neutral before they separate from each other.

Experiments were performed by the mass-analyzed ion kinetic energy spectrometry technique [5] using a VG ZAB-2HF mass spectrometer. The ions **1** and **2** were prepared by chemical ionization using various protonating agents in combination with deuterium and ^{13}C -labeling. Our results (Table 1) show that both **1** and **2** predominantly dissociate by loss of (H,C,N) to give C_3H_7^+ (m/z 43). The data of ^{13}C -labeling studies on $n\text{-C}_3\text{H}_7^{13}\text{CNH}^+$ establish that the ^{13}C atom is fully retained in the expelled (H,C,N) neutral. This

implies that there is no intramolecular rearrangement via cyclic intermediates prior to dissociation as we observed for CH_3CNH^+ [6].

The kinetic energy release, measured as $T_{0.5}$ [5] from the metastable peak width at half-height, for loss of (H,C,N) from **1** ($T_{0.5} = 36.9$ meV) is higher than from **2** ($T_{0.5} = 27.6$ meV). This effect is analogous to that found [4] for the $n\text{-C}_3\text{H}_7\text{CO}^+$ and $i\text{-C}_3\text{H}_7\text{CO}^+$ ions, and may be assigned to the isomerization of $n\text{-C}_3\text{H}_7^+$ to $i\text{-C}_3\text{H}_7^+$ before or during loss of (H,C,N) from **1**. This process is expected to occur when the interspecies distance in $[n\text{-C}_3\text{H}_7 \dots \text{CNH}]$ is lengthened to allow the isomerization (Ab initio calculations performed for $n\text{-C}_4\text{H}_{10}^+$ predict that isomerization of $n\text{-to-}i\text{-C}_3\text{H}_7^+$ occurs at a $[n\text{-C}_3\text{H}_7 \dots \text{CH}_3]$ separation of ca. 2.1 Å.) [7]. Relevant to the occurrence of ion-neutral complexes during dissociation of ions **1** and **2** is the formation of abundant $\text{C}_3\text{H}_6\text{D}^+$ (m/z 44) from $n\text{-C}_3\text{H}_7\text{CND}^+$ and $i\text{-C}_3\text{H}_7\text{CND}^+$ (Table 1), which indicates that loss of (H,C,N) is accompanied by a very large deuterium incorporation into the C_3H_7^+ product ion in both cases.

All these results can be explained by a mechanism illustrated in Scheme 1 which involves the intermediate formation of an ion-neutral complex **2a**, the $i\text{-C}_3\text{H}_7^+$ partner of which serves as a protonated reagent [the proton affinity $\text{PA}(\text{HNC}) > \text{PA}(\text{C}_3\text{H}_6)$, see [8a]] for HNC (**2a** $\rightarrow$ **2b**). The extensive (H,C,N) -to- C_3H_7 H/D exchange suggests that the interspecies separation in the ion-neutral complex **2b** is large enough to allow a reorientation of the partners into a configuration which permits D^+ -transfer from HCND^+ to $\text{CH}_3\text{CH} = \text{CH}_2$ [$\text{PA}(\text{HCN}) < \text{PA}(\text{C}_3\text{H}_6)$, see [8a]]. [$\Delta H_f(\text{C}_3\text{H}_6\text{CN}) = 45$ kcal/mol is estimated on the basis of $\Delta H_f(\text{C}_3\text{H}_6\text{CN}) = \Delta H_f(\text{C}_3\text{H}_7\text{CN}) - \Delta H_f(\text{H}) + \text{D}(\text{H-C}_3\text{H}_6\text{CN})$ (assuming $\text{D}(\text{H-C}_3\text{H}_6\text{CN})$ is that of $\text{D}(\text{H-CH}(\text{CH}_3)\text{CN}) \approx 90$ kcal/mol see [8b]) thermochemical data from ref. 8a].

This interpretation is in harmony with the low

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Table 1. Partial mass-analyzed ion kinetic energy spectra of the $n\text{-C}_3\text{H}_7\text{CNX}^+$ and $i\text{-C}_3\text{H}_7\text{CNX}^+$ ($X = \text{H}$ or D) metastable ions generated by the gas-phase reactions $\text{MX}^+ + \text{C}_3\text{H}_7\text{CN} \rightarrow \text{C}_3\text{H}_7\text{CNX}^+ + \text{M}$

Initial structure	MX ⁺	-H _r ^a (kcal/mol)	Mass to charge ratio of daughter ions ^b									
			27	28	29	39	40	41	42	43	44	
n-C ₃ H ₇ CNH ⁺	n-C ₃ H ₇ CN ⁺	49 ^c	4	8		3	2	9	2	70		
	SH ₃ ⁺	23	7	6	2	4	2	11	1	58		
n-C ₃ H ₇ ¹³ CNH ⁺	H ₃ ⁺	92	1		8			1	2	90		
	(CH ₃) ₂ OH ⁺	2	2		6			2	2	88		
n-C ₃ H ₇ CND ⁺	D ₃ ⁺	92			7			1	1	11	79	
	CD ₃ CND ⁺	2	3	2	7	4	1	4	7	15	50	
i-C ₃ H ₇ CNH ⁺	i-C ₃ H ₇ CN ⁺	49 ^c		2					1	97		
	SH ₃ ⁺	23	2	4		3		2	2	84		
i-C ₃ H ₇ CND ⁺	D ₃ ⁺	92								5	95	
	CD ₃ CND ⁺	2			4	1		1	2	5	85	

^a Nominal heat of reaction calculated by using the heats of formation taken from ref. 8a.

^b Intensities of peaks are expressed as percentage of the sum of intensities of the peaks due to daughter ions.

^c Nominal heat of reaction calculated by using the heats of formation taken from ref. 8a and the estimated heat of formation of $\text{C}_3\text{H}_6\text{CN}$ from page 178.

stabilization energy of $2b^1$. The interaction of $i\text{-C}_3\text{H}_7^+$ with HCN at moderate separations (3.5-5 Å) is expected to be in the range of 17-8 kcal/mol. Since the rearrangements of **1a** and **2a** into **2c** (Scheme 1) are exothermic,² it is very plausible that part of the complexes **2c** formed from both precursors will exceed the $i\text{-C}_3\text{H}_7^+ \cdots \text{NCH}$ bond strength leading to the product $i\text{-C}_3\text{H}_7^+ + \text{HCN}$. A fraction of the exothermicity appears as kinetic energies of these products. These are reflected in the $T_{0.5}$ values discussed above, where the higher $T_{0.5}$ value for **1** is in line with the higher energy content of complex **2c** when arising from **1**. Another argument for the occurrence of ion-neutral complexes in the dissociation of ions **1** and **2** is provided by the observed small yields of HCNH^+ (m/z 28) from unlabeled **1** and **2** as well as $\text{H}^{13}\text{CNH}^+$ and $(\text{H,C,N,D})^+$ (m/z 29) from the labeled precursors (Ta-

ble 1). They suggest that some of the ion-neutral complexes **2b** have sufficient energy to dissociate into the products $\text{HCNH}^+ + \text{C}_3\text{H}_6$.

Although ions **1** and **2** are isoelectronic with $n\text{-C}_3\text{H}_7\text{CO}^+$ and $i\text{-C}_3\text{H}_7\text{CO}^+$, the extension of our findings as an indication for the involvement of ion-neutral complexes in the unimolecular dissociation of the latter ions seems not to be straightforward because of the large differences in the dipole moments of HNC ($\mu = 2.65$ D), HCN ($\mu = 2.98$ D) and CO ($\mu = 0.10$ D) (see [9]).

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¹ Stabilization energies relative to the energies of the separated products for complexes **2b** and **2c** were estimated from the expression for ion-dipole interaction (see, for example, ref 2) using the dipole moments of 2.98 and 0.37 D for HCN and $\text{CH}_3\text{CH}=\text{CH}_2$, respectively, taken from ref 9. Complex **2b** is stabilized by 1.5 kcal/mol at a distance of 4 Å.

² The exothermicities of the rearrangement of **1a** and **2a** into **2c** calculated as the differences $\Delta H_f(n\text{-C}_3\text{H}_7^+ + \text{HNC}) - \Delta H_f(i\text{-C}_3\text{H}_7^+ + \text{HCN}) = 36$ kcal/mol and $\Delta H_f(i\text{-C}_3\text{H}_7^+ + \text{HNC}) - \Delta H_f(i\text{-C}_3\text{H}_7^+ + \text{HCN}) = 16$ kcal/mol, respectively. The heats of formation were taken from ref 8a.