Ion-neutral complexes in gas-phase dissociations of protonated nitriles: n-C3H7CNH+ and i-C3H7CNH+

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Instytut Chemii Fizycznej PAN
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Ion-Neutral Complexes in Gas-Phase Dissociations of Protonated Nitriles: n-C$_3$H$_7$CNH$^+$ and i-C$_3$H$_7$CNH$^+$

H. Wincel

Polish Academy of Science, Institute of Physical Chemistry, Warszawa, Poland

R. H. Fokkens and N. M. M. Nibbering

Institute of Mass Spectrometry, University of Amsterdam, Amsterdam, The Netherlands

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-C$_3$H$_7$R$^+$ and i-C$_3$H$_7$R$^+$, where a.o. R = CH$_2$O, CH$_3$CHO and (CH$_3$)$_2$CO [2], CH$_2$ = NH [3a] and CH$_3$CH = NH [3b] and CO [4], ion-neutral complexes have been invoked to rationalize the intramolecular isomerization of [n-C$_3$H$_7^+$ . . . R] into [i-C$_3$H$_7^+$ . . . R] before elimination of R or, in appropriate systems, the derived alkene(R-H) [2–4]. However, for R = CO the presumed involvement of such complexes is very difficult to verify experimentally, as in that case a possible interaction between the C$_3$H$_7^+$ 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-C$_3$H$_7$CNH$^+$, 1, and i-C$_3$H$_7$CNH$^+$, 2, which are iso-electronic with n-C$_3$H$_7$CO$^+$ and i-C$_3$H$_7$CO$^+$, respectively. The proton (deuteron) on nitrogen in these ions serves as a valuable tool to probe the interaction between the C$_3$H$_7^+$ 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$_3$H$_7^+$ (m/z 43).The data of ^{13}C-labeling studies on n-C$_3$H$_7$^{13}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$_3$CNH$^+$ [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-C$_3$H$_7$CO$^+$ and i-C$_3$H$_7$CO$^+$ ions, and may be assigned to the isomerization of n-C$_3$H$_7^+$ to i-C$_3$H$_7^+$ before or during loss of (H,C,N) from 1. This process is expected to occur when the interspecies distance in [n-C$_3$H$_7^+$ . . . CNH] is lengthened to allow the isomerization (Ab initio calculations performed for n-C$_4$H$_{10}^{+\cdot}$ predict that isomerization of n-to-i-C$_3$H$_7^+$ occurs at a [n-C$_3$H$_7^+$ . . . CH$_3$] separation of ca. 2.1 Å.) [7]. Relevant to the occurence of ion-neutral complexes during dissociation of ions 1 and 2 is the formation of abundant C$_3$H$_6$D$^+$ (m/z 44) from n-C$_3$H$_7$CND$^+$ and i-C$_3$H$_7$CND$^+$ (Table 1), which indicates that loss of (H,C,N) is accompanied by a very large deuterium incorporation into the C$_3$H$_7^+$ product ion in both cases.
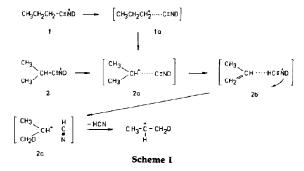
All these results can be explained by a mechanism illustrated in Scheme I which involves the intermediate formation of an ion-neutral complex 2a, the i-C$_3$H$_7^+$ partner of which serves as a protonated reagent [the proton affinity PA(HNC) > PA(C$_3$H$_6$), see [8a]] for HNC (2a → 2b). The extensive (H,C,N)-to-C$_3$H$_7$ 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 CH$_3$CH = CH$_2$[PA(HCN) < PA(C$_3$H$_6$), see [8a]]. [ΔH$_f$ (C$_3$H$_6$CN) = 45 kcal/mol is estimated on the basis of ΔH$_f$(C$_3$H$_6$CN) = ΔH$_f$(C$_3$H$_7$CN) − ΔH$_f$(H) + D(H-C$_3$H$_6$CN) (assuming D(H-C$_3$H$_6$CN) is that of D(H-CH(CH$_3$)CN) ≈ 90 kcal/mol see [8b]) thermochemical data from ref. 8a].

This interpretation is in harmony with the low

Table 1. Partial mass-analyzed ion kinetic energy spectra of the n-$C_3H_7CNX^+$ and i-$C_3H_7CNX^+$ ($X = H$ or D) metastable ions generated by the gas-phase reactions $MX^+ + C_3H_7CN \rightarrow C_3H_7CNX^+ + M$

Initial structure	MX$^+$	$-H_r^a$ (kcal/mol)	Mass to change ratio of daughter ions^b								
			27	28	29	39	40	41	42	43	44
n-$C_3H_7CNH^+$	n-$C_3H_7CN^+$	49^c	4	8		3	2	9	2	70	
	SH_3^+	23	7	6	2	4	2	11	1	58	
n-$C_3H_7{}^{13}CNH^+$	H_3^+	92	1		8			1	2	90	
	$(CH_3)_2OH^+$	2	2		6			2	2	88	
n-$C_3H_7CND^+$	D_3^+	92			7			1	1	11	79
	CD_3CND^+	2	3	2	7	4	1	4	7	15	50
i-$C_3H_7CNH^+$	i-$C_3H_7CN^+$	49^c		2					1	97	
	SH_3^+	23	2	4		3		2	2	84	
i-$C_3H_7CND^+$	D_3^+	92								5	95
	CD_3CND^+	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 C_3H_6CN from page 178.

Scheme I

stabilization energy of **2b**[1]. The interaction of i-$C_3H_7^+$ 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 I) are exothermic,[2] it is very plausible that part of the complexes **2c** formed from both precursors will exceed the i-$C_3H_7^+$ ... NCH bond strength leading to the product i-$C_3H_7^+$ + 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 $H^{13}CNH^+$ and $(H,C,N,D)^+$ (m/z 29) from the labeled precursors (Ta-

ble 1). They suggest that some of the ion-neural complexes **2b** have sufficient energy to dissociate into the products $HCNH^+ + C_3H_6$.

Although ions **1** and **2** are isoelectronic with n-$C_3H_7CO^+$ and i-$C_3H_7CO^+$, 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 of the dipole moments of HNC ($\mu = 2.65$ D), HCN ($\mu = 2.98$ D) and CO ($\mu = 0.10$ D) (see [9]).

Acknowledgments

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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 $CH_3CH = CH_2$, 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 $\Delta H_f(n$-$C_3H_7^+ + HNC) - \Delta H_f(i$-$C_3H_7^+ + HCN) = 36$ kcal/mol and $\Delta H_f(i$-$C_3H_7^+ + HNC) - \Delta H_f(i$-$C_3H_7^+ + HCN) = 16$ kcal/mol, respectively. The heats of formation were taken from ref 8a.