Tetrahedron Letters,Vol.25,No.8,pp 893-896,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

Isomers of Amine Molecular Ions; The Structures of $C_2H_7N^{+\cdot}$ and Related Radical Cations

STEEN HAMMERUM, DIETMAR KUCK, and PETER J. DERRICK

Department of General and Organic Chemistry, University of Copenhagen,
The H.C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark;
Fakultät für Chemie, Universität Bielefeld, 4800 Bielefeld 1, FRG;
School of Chemistry, University of New South Wales, Kensington NSW 2033, Australia

Dedicated to Professor Carl Djerassi on the occasion of his 60th birthday

Abstract. $[CH_3CHNH_3]^{+\cdot}$ and $[CH_2CH_2NH_3]^{+\cdot}$ ions exist as distinct, stable species in the gas-phase. These ions are formed from a variety of precursors, and they can be characterized by their unimolecular and collision-induced reactions. The properties of deuterium labeled analogs confirm the proposed structures. Evidence that stable $C_3H_9N^{+\cdot}$ ions with unconventional structures also exist is presented; these and other amine ion isomers are formed from, *inter alia,* alkylamine molecular ions in the ion source.

Isomerism in cation-radicals is considerably more extensive than in neutral species, in the sense that the structure of many a stable cation-radical does not correspond to that of a stable neutral molecule. Such ions with unconventional structures exist besides the more common molecular ions formed by removal of an electron from stable molecules and may even be more stable than these. Early members of this family of unusual ions include **1** and **2**, isomers of methanol and methylamine, formed by radiolysis and characterized by ESR spectroscopy.[1,2]

$\cdot CH_2OH_2^+$ **1** $\qquad$ $\cdot CH_2NH_3^+$ **2**

The results of semi-empirical and *ab initio* calculations[3-5] indicate that two-carbon cation-radicals with the structures below will exist in potential wells, and that these ions may even be of lower energy than the conventional $C_2H_5X^{+\cdot}$ molecular ions. The present study and other very recent work[5-10] has verified the existence of a number of these species in the gas-phase.

$$[CH_3CHXH]^{+\cdot} \qquad [CH_2CH_2XH]^{+\cdot} \qquad [CH_3XCH_2]^{+\cdot} \qquad X = OH,\ NH_2,\ PH_2,\ \text{halogen}$$

Ab initio calculations[11] suggest that at least five $C_2H_7N^{+\cdot}$ isomers should exist as stable, independently observable species. Two of these, $CH_3CH_2NH_2^{+\cdot}$ (**3**) and $(CH_3)_2NH^{+\cdot}$ (**4**), have stable neutral counterparts. Holmes and coworkers[10] have shown that a $C_2H_7N^{+\cdot}$ ion different from **3** and **4** is formed by loss of $CH_2=NH$ from the molecular ion of 1,3-propandiamine; they suggested that *"the new ion is best represented by* $[CH_2CH_2NH_3]^{+\cdot}$". Previously, it has been speculated[12] that the $C_2H_7N^{+\cdot}$ ions formed by alkene elimination from *n*-alkylamine molecular ions have either structure **5** or **6**, and loss of benzaldehyde from benzyloxyethylamine produces $C_2H_7N^{+\cdot}$ ions that have been described as **5**.[13]

$CH_3CH_2NH_2^{+\cdot}$ **3** $\qquad$ $(CH_3)_2NH^{+\cdot}$ **4** $\qquad$ $[CH_2CH_2NH_3]^{+\cdot}$ **5** $\qquad$ $[CH_3CHNH_3]^{+\cdot}$ **6**

$[CH_2CH_2NH_3]^{+\cdot}$ Ions of m/z 45 ($C_2H_7N^{+\cdot}$) are observed in the electron impact mass spectra of 1,3-propandiamine (loss of $CH_2{=}NH$), 3-aminopropanol (loss of CH_2O), *n*-alkylamines (loss of alkene molecules), and 2-benzyloxyethylamine (loss of C_6H_5CHO).

$$\begin{array}{lcccl} C_4H_9CH_2CH_2NH_2^{+\cdot} & \rightarrow & & \leftarrow & HOCH_2CH_2CH_2NH_2^{+\cdot} \\ & & C_2H_7N^{+\cdot} & & \\ NH_2CH_2CH_2CH_2NH_2^{+\cdot} & \rightarrow & & \leftarrow & C_6H_5CH_2OCH_2CH_2NH_2^{+\cdot} \end{array}$$

We find that these $C_2H_7N^{+\cdot}$ ions all have the same structure. Their metastable ion spectra are simple and almost superimposable. They consist of peaks at m/z 30 and m/z 18, in a ratio of *circa* 3:1, corresponding to loss of $CH_3^{\cdot}$ and $C_2H_3^{\cdot}$. The collision-induced reactions of these $C_2H_7N^{+\cdot}$ ions are also virtually identical, and they all produce doubly-charged ions (m/z 22½) by charge stripping. The reactions demonstrate that these $C_2H_7N^{+\cdot}$ ions are different from **3** and **4**; Holmes *et al.*[10] have recently shown this to be the case for the $C_2H_7N^{+\cdot}$ ions formed from 1,3-propandiamine.

$$CH_3^{\cdot} + CH_2{=}NH_2^{+} \leftarrow \underset{\mathbf{5}}{{}^{\cdot}CH_2CH_2NH_3^{+}} \rightarrow C_2H_3^{\cdot} + NH_4^{+}$$

Structure **5** is assigned to these ions, in good agreement with their formation and fragmentation reactions. The isotopic specificity (see Table) of these reactions for the $C_2H_7N^{+\cdot}$ analogs derived from deuterium labeled precursors seems to rule out any alternative structure.

Unimolecular reactions (μsec timeframe) of deuterium labeled $C_2H_7N^{+\cdot}$ ions (**5**).

precursor	*putative structure*	*ionic products*	
unlabeled	${}^{\cdot}CH_2CH_2NH_3^+$	$CH_2{=}NH_2^+$	NH_4^+
$DOCH_2CH_2CH_2ND_2$	${}^{\cdot}CH_2CH_2ND_3^+$	$CH_2{=}ND_2^+$	NHD_3^+
$RCH_2CD_2NH_2$ $RCD_2CH_2NH_2$	${}^{\cdot}CH_2CD_2NH_3^+$ ${}^{\cdot}CD_2CH_2NH_3^+$	$CH_2{=}NH_2^+$, $CD_2{=}NH_2^+$	NH_3D^+, NH_4^+

MIKE spectra recorded on an unusually large double-focusing mass spectrometer of reversed geometry (University of New South Wales) and on a VG ZAB-2F instrument (Universität Bielefeld).

The unimolecular reactions require transfer of a hydrogen atom from carbon to nitrogen (loss of $C_2H_3^{\cdot}$) or from nitrogen to carbon (loss of $CH_3^{\cdot}$). There are pronounced isotope effects on these reactions: the ratio of $CH_2D^{\cdot}$ loss to $C_2H_3^{\cdot}$ loss is 1:5 for $[CH_2CH_2ND_3]^{+\cdot}$ ions, whereas the ratio for the unlabeled ions is 3:1. Correspondingly, $[CH_2CH_2NHD_2]^{+\cdot}$ ions lose $CH_3^{\cdot}$ and $CH_2D^{\cdot}$ in a 7:2 ratio, where 1:2 is the statistically expected value. For $[CH_2CH_2NH_2D]^{+\cdot}$ ions the observed ratio is *circa* 10. There is also considerable discrimination against deuterium in the carbon-to-nitrogen hydrogen transfer: the m/z 18 : m/z 19 ratio for $[CH_2CD_2NH_3]^{+\cdot}$ (or $[CD_2CH_2NH_3]^{+\cdot}$, see below) is 3.3.

The unimolecular as well as the collision induced reactions of the $C_2H_5D_2N^{+\cdot}$ ions formed from α- and β-deuterated alkylamines are very nearly identical; in particular, the unimolecular methyl loss is in both cases specifically elimination of $CH_3^{\cdot}$ and $CHD_2^{\cdot}$ in a ratio of 4:3 (no loss of $CH_2D^{\cdot}$). This shows that the carbon atoms become equivalent prior to fragmentation, which requires that rapid NH_3-shifts take place between the two carbon atoms in **5** and verifies Radom's prediction[3] that the energy barrier should be low for the degenerate 1,2-NH_3 shift.[14]

$${}^{\cdot}CH_2CD_2NH_3^+ \rightleftarrows {}^{\cdot}CD_2CH_2NH_3^+$$

$[CH_3CHNH_3]^{+\cdot}$ $C_2H_7N^{+\cdot}$ ions are also formed, albeit in very low ion yield, from 2-aminopropanol, 1,2-propandiamine, and 2,3-butandiamine. The analogy to the reactions that lead to $\cdot CH_2NH_3^+$ ions (**2**) (*e.g.*, loss of CH_2O from $HOCH_2CH_2NH_2^{+\cdot}$)[7,10,15] suggests that this $C_2H_7N^{+\cdot}$ ion is the higher homolog, **6**. This is in good agreement with the fragmentation reactions observed.

$$CH_3CH(NH_2)CH_2OH^{+\cdot} \quad \rightarrow \quad \underset{\textbf{6}}{CH_3CHNH_3^+} \quad \rightarrow \quad CH_4N^+,\ NH_4^+$$

Interference from the ^{13}C isotope of the very abundant α-cleavage ion ($C_2H_6N^+$) precludes satisfactory characterization of these $C_2H_7N^{+\cdot}$ ions, but their presence is readily recognized since the metastable ion spectrum of m/z 45 shows a strong peak corresponding to elimination of $CH_3^\cdot$. Further, doubly-charged ions (m/z 22½) are formed by collision of the m/z 45 ions with He atoms. The α-cleavage ion does not undergo similar reactions. Unambiguous characterization is, however, possible for the trideuterated ions, $C_2H_4D_3N^{+\cdot}$, formed after exchange of H for D in the -OH and $-NH_2$ groups of the parent molecules, since these ions are two mass units heavier than the α-cleavage ions.[16] The unimolecular reactions as well as the collision induced reactions observed for the -d_3 ions are considerably different from those of the $[CH_2CH_2ND_3]^{+\cdot}$ ions described above, as well as from those of **3** or **4**. In particular, $[CH_3CHND_3]^{+\cdot}$ loses $CH_3^\cdot$ in both unimolecular and collision induced reactions, where $[CH_2CH_2ND_3]^{+\cdot}$ eliminates $CH_2D^\cdot$; (partial) hydrogen exchange prior to fragmentation leads to formation of NHD_3^+ and $NH_2D_2^+$ ions, where $[CH_2CH_2ND_3]^{+\cdot}$ produces NHD_3^+ ions nearly exclusively. Furthermore, **6** readily loses H· and H_2 in the unimolecular and collision induced processes; the corresponding reactions do not give rise to abundant ions for **5**.

Homologous Ions. Loss of C_3H_6 from 2-methylpentylamine produces $C_3H_9N^{+\cdot}$ ions. This reaction is analogous to the formation of **5** by β-cleavage after hydrogen rearrangement of straight-chain primary amine molecular ions, and these ions are by analogy assigned structure **7**.

$$CH_3CH_2CH_2CH(CH_3)CH_2NH_2^{+\cdot} \rightarrow CH_3CHCH_2CH(CH_3)CH_2NH_3^+ \rightarrow \underset{\textbf{7}}{CH_3CHCH_2NH_3^+} + C_3H_6$$

Unimolecular fragmentation of **7** leads primarily to NH_4^+ ions. The collision induced reactions also lead, *inter alia*, to loss of NH_3 and to doubly-charged ions, m/z 29½. These reactions are different from those of the molecular ions of the four C_3 amines; in particular, neither loss of H·, $CH_3^\cdot$, nor $C_2H_5^\cdot$ is a prominent reaction of ion **7**.

Also γ-cleavage after hydrogen rearrangement is observed for primary amines. For *n*-alkylamines this leads to another $C_3H_9N^{+\cdot}$ isomer:

$$CH_3(CH_2)_4CH_2NH_2^{+\cdot} \quad \rightarrow \quad \underset{\textbf{8}}{\cdot CH_2CH_2CH_2NH_3^+} \quad \rightarrow \quad \underset{\textbf{9}}{CH_3CH_2CH_2NH_2^{+\cdot}}$$

The predominant unimolecular reaction of these $C_3H_9N^{+\cdot}$ ions is loss of $C_2H_5^\cdot$, suggesting reaction *via* rearrangement to **9**. However, comparison of the collision induced reactions with those of propylamine molecular ions shows that at least some of the $C_3H_9N^{+\cdot}$ ions formed from, *e.g.*, hexylamine have a different structure. Structure **8** is proposed for these ions, based on their mode of formation and on the collision induced loss of C_2H_4 (the $\cdot CH_2CD_2CH_2NH_3^+$ ions formed from hexylamine-2,2-d_2 correspondingly lose $C_2H_2D_2$).

Our attempts to identify **6** and the fifth $C_2H_7N^{+\cdot}$ isomer, $[CH_3NH_2CH_2]^{+\cdot}$, among the odd-electron ions formed from primary and secondary alkylamines have failed so far. However, primary alkylamine molecular ions fragment to give $CH_5N^{+\cdot}$ ions (*m/z* 31) in appreciable abundance. The collision induced reactions of these ions show that they are of structure **2** rather than methylamine molecular ions. α-Labeled primary amine ions, $RCD_2NH_2^{+\cdot}$, correspondingly form $\cdot CD_2NH_3^+$. The collision induced reactions of these ions are as expected from the work of Holmes and coworkers.[7,10,15] In particular, the *m/z* 14 product ion formed from the unlabeled species is cleanly shifted to *m/z* 16.

References and Notes

1 D.R.G. Brimage, J.D.P. Cassell, J.H. Sharp, and M.C.R. Symons, *J. Chem. Soc. A*, **1969**, 2619

2 R.P. Kohin and P.G. Nadeau, *J. Chem. Phys.*, **44**, 691 (1966)

3 B.T. Golding and L. Radom, *J. Am. Chem. Soc.*, **98**, 6331 (1976)

4 W.J. Bouma, R.H. Nobes, and L. Radom, *J. Am. Chem. Soc.*, **105**, 1743 (1983)

5 Y. Apeloig, B. Ciommer, G. Frenking, M. Karni, A. Mandelbaum, H. Schwarz, and A. Weisz, *J. Am. Chem. Soc.*, **105**, 2186 (1983)

6 J.K. Terlouw, W. Heerma, and G. Dijkstra, *Org. Mass Spectrom.*, **16**, 326 (1981)

7 J.L. Holmes, F.P. Lossing, J.K. Terlouw, and P.C. Burgers, *J. Am. Chem. Soc.*, **104**, 2931 (1982)

8 J.L. Holmes, P.C. Burgers, J.K. Terlouw, H. Schwarz, B. Ciommer, and H. Halim, *Org. Mass Spectrom.*, **18**, 208 (1983)

9 E. Weger, K. Levsen, I. Ruppert, P.C. Burgers, and J.K. Terlouw, *Org. Mass Spectrom.*, **18**, 327 (1983)

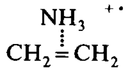
10 J.L. Holmes, F.P. Lossing, J.K. Terlouw, and P.C. Burgers, *Can. J. Chem.*, **61**, 2305 (1983)

11 Unpublished work by W.J. Bouma, J.M. Dawes, and L. Radom

12 S. Hammerum, J.B. Christensen, H. Egsgaard, E. Larsen, K.F. Donchi, and P.J. Derrick, *Int. J. Mass Spectrom. Ion Phys.*, **47**, 351 (1983)

13 G. Eckhardt, *Org. Mass Spectrom.*, **14**, 31 (1979)

14 An alternative interpretation is that **5** is not the end-on complex of ethylene and ammonia (less one electron), but rather the symmetrical species, **5'**. However, calculations[4] have shown that the corresponding ion in the analogous oxygen system (ethylene – water) does not correspond to a minimum on the energy hyper-surface; **5'** will, however, be an intermediate or transition-state in the degenerate 1,2-NH_3-shift in **5**.



$$\overset{NH_3}{CH_2{=}CH_2}^{+\cdot}$$

5'

15 J.K. Terlouw, W. Heerma, G. Dijkstra, J.L. Holmes, and P.C. Burgers, *Int. J. Mass Spectrom. Ion Phys.*, **47**, 147 (1983)

16 Close examination of the ions formed after deuterium exchange reveals that some of the $C_2H_6N^+$ ions incorporate three exchangeable hydrogen atoms, that is, these ions are not exclusively $CH_3CH=NH_2^+$, some $CH_2=CHNH_3^+$ ions must also be present. In particular, collisional activation of the *m/z* 47 ions formed from, *e.g.*, $CH_3CH(NH_2)CH_2OH$ after exchange deuteration in the mass spectrometer inlet leads, *inter alia*, to *m/z* 21 ions (NHD_3^+). This, of course, is a possible reaction for $CH_2=CHND_3^+$, but not for the two other *m/z* 47 ions present, $CH_3CHNHD_2^{+\cdot}$ and $[U\text{-}^{13}C]CH_3CH=ND_2^+$. Holmes and Terlouw have also observed $CH_2=CHNH_3^+$ ions (J.L. Holmes, personal communication), and these ions have been included in computational studies (M.R. Ellenberger, R.A. Eades, M.W. Thomsen, W.E. Farneth, and D.A. Dixon, *J. Am. Chem. Soc.*, **101**, 7151 (1979), and R.A. Eades, D.A. Weil, M.R. Ellenberger, W.E. Farneth, D.A. Dixon, and C.H. Douglass, *J. Am. Chem. Soc.*, **103**, 5372 (1981)).

(Received in UK 19 December 1983)