

## Intramolecular Hydrogen Atom Abstraction with an Eight-Membered Cyclic Transition State in Open-Chain Aliphatic Aminium Radicals

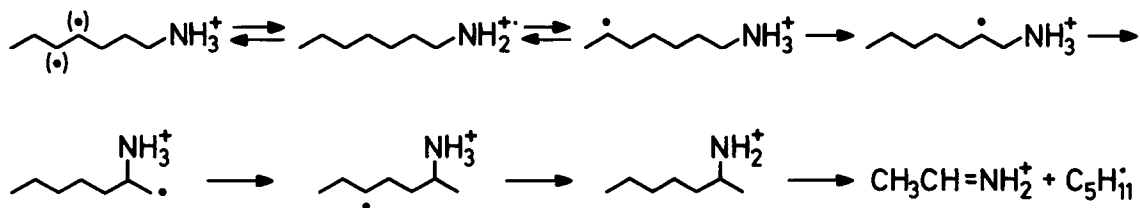
GEORGES SOZZI, JEAN-PIERRE DENHEZ, HENRI EDOUARD AUDIER,\*  
TORE VULPIUS, and STEEN HAMMERUM\*

*Laboratoire de Synthèse Organique, Ecole Polytechnique, F-91128 Palaiseau, France, and Department of General and Organic Chemistry, University of Copenhagen, The H.C. Ørsted Institute, DK-2100 Copenhagen, Denmark*

**Abstract.** Hydrogen abstraction by the nitrogen in long-chain aliphatic gas-phase aminium radicals (amine molecular ions) takes place via six-, seven-, and eight-membered cyclic transition states. The subsequent fragmentation is particularly facile after eight-membered ring hydrogen transfer.

Intramolecular hydrogen atom transfer from an aliphatic chain to the  $-NHR^{\cdot}$  in aminium radicals is the key step in the Hofmann-Löffler reaction. The hydrogen abstraction occurs preferentially via a six-atom cyclic transition state;<sup>1,2</sup> similar selectivity is observed for most condensed-phase intramolecular hydrogen atom transfer reactions. The prevalence of six-membered transition states (over transition states with seven or eight members) is often ascribed to entropic factors (loss of rotational degrees of freedom), and it has been suggested that hydrogen abstraction at more remote positions could be due to inter- rather than intramolecular processes.<sup>3</sup> Intramolecular hydrogen atom abstraction in aliphatic aminium radicals also occurs in the gas phase, where it has been shown to be reversible,<sup>4</sup> in contrast to the solution reaction.<sup>2</sup> The present results unequivocally demonstrate that hydrogen atom transfer from an aliphatic chain to nitrogen in aminium radicals in the gas phase can take place via six-, seven-, as well as eight-membered cyclic transition states.

Aminium radicals — amine molecular ions — can be generated efficiently in a mass spectrometer ion source. The conventional mass spectra of alkylamines show that reactions other than simple cleavage of the  $\alpha$ -C-C bond do not occur to any great extent in the ion source after ionization with 70 eV electrons.<sup>5</sup> However, simple cleavage is favored only for the very fast reactions of relatively high internal energy amine ions. Rearrangement reactions and hydrogen abstraction precede fragmentation when slow reactions (on the mass spectrometer time-scale) of low-energy primary aminium ions are observed (metastable ions, MIKE spectra).<sup>4,6</sup> The predominant reaction under these conditions leads to  $C_2H_6N^+$  ions (see Scheme). The key step is abstraction of a hydrogen atom at C2, initiating migration of  $NH_3$  from C1 to C2. Fast and reversible intramolecular hydrogen abstraction/exchange precedes this step, leading to loss of positional identity for the hydrogen atoms of the amino and methylene groups involved in the exchange. The extent of CH/NH exchange can be determined from the deuterium incorporation in the fragment ions formed from specifically labeled heptylamine ions (Table).



**Table.**  $C_2(H,D)_6N^+$  Ions<sup>a</sup> formed from deuterium labeled heptylamine molecular ions.<sup>b</sup>

$m/z$	heptylamine-									hexylamine-	octylamine-
	$d_0$	1,1- $d_2$	2,2- $d_2$	3,3- $d_2$	4,4- $d_2$	5,5- $d_2$	6,6- $d_2$	7,7,7- $d_3$	$N,N$ - $d_2$	$N,N$ - $d_2$	$N,N$ - $d_2$
44	100	2	18	89	39	38	32	95	41	36	42
45		21	71	11	52	51	55	5	50	51	49
46		77	11		9	11	13		9	13	9

(a) These carry more than 95% of the fragmenting ion current; abundances given in % of the combined abundance of the  $m/z$  44-46 ions. (b) MIKE spectra, measured on a VG ZAB-2F mass spectrometer.

The deuterium incorporation in the product ions shows that all eight hydrogen atoms initially located at N, C4, C5, and C6 are extensively involved in CH/NH exchange prior to fragmentation. Three of these hydrogen atoms are incorporated in the product ion. The slight deviation from the label distribution expected for incorporation of three hydrogen (deuterium) atoms taken at random from two D plus six H (36:54:11) is caused by side reactions involving the C1-C3 hydrogen atoms. Increasing chain length does not increase the number of hydrogen atoms involved in the exchange reactions (compare heptyl- and octylamine- $N,N$ - $d_2$ ). The exchange reactions are fast compared with the subsequent cleavage, and an equilibrium-type situation with regard to the -NH<sub>2</sub> and the C4, C5, and C6 CH<sub>2</sub> groups has apparently been reached. Increasing reaction time does not change the label distribution for  $N$ -deuterated ions, whereas increased exchange is observed for C1 and C2 labeled ions, demonstrating that the reactions involving these positions are much slower.

The slightly high incorporation of deuterium atoms observed for heptylamine-6,6- $d_2$  indicates that abstraction of the C2 hydrogen is particularly facile after transfer of a C6 hydrogen to N. This is supported by the observation that hexylamine-2,2- $d_2$  generates  $m/z$  45 ions nearly exclusively (the  $m/z$  44:45:46 ratio is 2:94:4). Hydrogen abstraction from C2 is in this case effectively irreversible (*cf.* heptylamine-2,2- $d_2$ ), which suggests that it is effected by the terminal methyl group. Preliminary RRKM calculations show that 1,7 hydrogen atom transfer is about two orders of magnitude slower than 1,5 transfer, but easily rapid enough to occur before the ions reach the second field-free region.

The present results thus provide firm evidence that intramolecular hydrogen abstraction by the nitrogen in aminium radicals with an eight-membered ring transition state is fast and efficient, and that this reaction in particular facilitates the subsequent rearrangement and fragmentation.

#### References

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