Loss of Methyl Radical From Some Small Immonium Ions: Unusual Violation of the Even-electron Rule

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Several small immonium ions of general formula $R^1R^2C = NR^3CH_3$ (R^1 , R^2 , $R^3 = H$ or alkyl) eliminate 'CH₃; this reaction occurs in the mass spectrometer in both fast (source) and slow (metastable) dissociations. Such behaviour violates the even-electron rule, which states that closed-shell cations usually decompose to give closed-shell daughter ions and neutral molecules. The heats of formation of the observed product ions (for example, $[(CH_3)_2C = NH]^+$) can be bracketed using arguments based on energy data. Deuterium labelling results reveal that the methyl group originally bound to nitrogen is not necessarily lost in the course of dissociation. Thus, for instance, $(CH_3)_2C = NHCD_3$ eliminates both CH_3 ' and CD_3 ', via different mechanisms, but very little CH_2D' or CHD_2' loss occurs.

According to the even-electron rule,¹ closed-shell cations normally decompose by loss of a neutral molecule, thus producing a closed-shell daughter ion; elimination of a radical, to form a radical cation, is observed only infrequently. The origins of this general rule are chiefly energetic in nature: closed-shell ions (and neutrals) possess an inherent stability that is absent in open-shell ions and radicals. Consequently, the even-electron rule is violated only when there are particular structural features stabilizing the radical cations so formed.² When small ions are considered, particularly where energy factors are dominant in determining relative fragmentation rates, as in metastable transitions,^{3,4} extensive loss of radicals from even-electron ions is extremely uncommon.

In the course of a systematic study of numerous immonium ions, CH_3 loss was detected in significant abundance from $CH_3CH_2CH=\dot{N}(CH_3)_2$, even in metastable transitions.⁵ Subsequent investigation reveals that CH_3 loss occurs in metastable transitions from $CH_3CH_2CH=\dot{N}HCH_3$ and $(CH_3)_2C=\dot{N}HCH_3$. These reactions all break the even-electron rule; presumably, the ionized imines produced by CH_3 elimination are relatively stable, thus accounting for the violation of the rule. However, no significant analagous loss of H⁻ is observed in slow reactions of the lower homologues $CH_3CH_2CH=\dot{M}H_2$ and $(CH_3)_2C=\dot{M}H_2$.⁶ These data, taken together with other information concerning the energetics of alternative dissociation routes, allow limits to be set for the heats of formation of several ionized imines.

Both $(CH_3)_2C = \ddot{N}HCH_3$ (a) and $CH_3CH_2CH = \ddot{N}HCH_3$ (b) undergo five significant slow reactions as given in Table 1.

Loss of CH₃NH₂ from $[C_4H_{10}N]^+$ gives rise to $[C_3H_5]^+$; assuming the daughter ion has the most stable structure, allyl cation, $\Sigma\Delta H_f^\circ$ (products) = 946 (allyl cation⁷)+(-21) (CH₃NH₂⁸) = 925 kJ mol⁻¹.

Table 1. Slow reactions of CH₃CH₂CH=-NHCH₃ and (CH₃)₂C=-NHCH₃

	Neutral lost ^a				
lon	H ₂	CH₃	C₂H₄	CH ₃ NH ₂	C₃He
(CH ₃) ₂ C—ŇHCH ₃ (a)	60	12	7	4	17
$CH_3CH_2CH = \hbar HCH_3 (b)$	14	12	28	9	37

^a Values measured by second field free region metastable peak areas and normalized to a total metastable ion current of 100 units.

Since $\Delta H_f^{\circ}(CH_3^{-}) = 142 \text{ kJ mol}^{-1,8}$ the observation that both CH_3NH_2 and CH_3^{-} are lost from *a* in similar abundances leads to the conclusion that $\Delta H_f^{\circ}((CH_3)_2C=NH^{++}) \approx 925 - 142 = 783 \text{ kJ mol}^{-1}$.

Cleavage of a N—H bond in $(CH_3)_2C=\bar{N}H_2$ would also produce $[(CH_3)_2C=NH]^{++}$; however, this process is not observed to a significant extent in metastable transitions;⁶ instead, NH₃ and C₂H₄ eliminations dominate. Loss of NH₃ gives rise to products having $\Sigma\Delta H_f^\circ = 946 - 46 \text{ kJ mol}^{-1}$, but probably involves a transition state with slightly higher energy (c. 920 kJ mol⁻¹).⁹ Elimination of C₂H₄ is also thought to proceed via a transition state having an energy of ~920 kJ mol⁻¹.⁹ Since $\Delta H_f^\circ(H^-) = 218 \text{ kJ mol}^{-1}$,⁸ the non-occurrence of H⁻ loss indicates that $\Delta H_f^\circ([CH_3)_2C=NH]^{+-})$ is greater than c. 920-218 = 702 kJ mol⁻¹.

Elimination of C_2H_4 from *a* and *b* probably proceeds by the mechanisms given in Scheme 1; these routes are analogous to those postulated for the lower homologues $(CH_3)_2C = NH_2$ and $CH_3CH_2CH = NH_2$.⁹ The highest energy species involved in Scheme 1 are the open-chain primary carbonium ions *c* and *e*. An isodesmic substitution procedure¹⁰ may be employed to estimate $\Delta H_f^{\circ}(c)$ and $\Delta H_f^{\circ}(e)$ as 900 and 879 kJ mol⁻¹ respectively. This leads to the



conclusion that $\Delta H_{f}^{\circ}([(CH_{3})_{2}C=NH]^{+}) = 900 - 142 = 758 \text{ kJ mol}^{-1}$, because both $C_{2}H_{4}$ and CH_{3}^{-1} losses are observed from *a*.

The above arguments suggest that $\Delta H_{\rm f}^{\circ}([(CH_3)_2C=$ NH]⁺⁻) is in excess of ~703 kJ mol⁻¹ and probably in the region 757–782 kJ mol⁻¹. Similar conclusions can be inferred concerning $\Delta H_{\rm f}^{\circ}([CH_3CH_2CH=$ NH]⁺⁻) by analogous reasoning.

The above analysis assumes that CH₃ loss can occur from a and b; essentially without reverse activation energy, by direct cleavage of the N-CH₃ bond. Deuterium labelling experiments support this hypothesis; thus, $(CH_3)_2C=NHCD_3$ $(a-d_3)$ and $CH_3CH_2CH=NHCD_3$ $(b-d_3)$ both lose CD_3 in metastable transitions. However, these ions also eliminate CH₃ in abundance approximately equal to CD₃ loss with only a minor amount of CD_2H or CH_2D loss. Moreover, loss of CH₃ and CD₃ occur via separate mechanisms because the associated metastable peaks have different kinetic energy releases. For example, loss of CH₃ and CD₃ from $a - d_3$ are characterized by kinetic energy releases $(T_{1/2})$ of 34 and 39 meV respectively; this relatively small, but distinctive, difference was repeatedly observed on two different instruments. Thus the surprising loss of CH₃ from $a-d_3$ and $b-d_3$ does not invalidate the energetics arguments given above. A possible explanation for the unexpected CH3 loss from these ions involves the formation of ionized vinyl methyl amine, Scheme 2.



Scheme 2

If this explanation is correct, the occurrence of both CH₃[•] and CD₃[•] loss from $a-d_3$ and $b-d_3$ indicates that $\Delta H_f^{\circ}([CH_2=CHNHCH_3]^{+\cdot})$ and

 $\Delta H_{\rm f}^{\circ}([CH_3CH_2CH=NH]^+)$ are (i) approximately equal, and (ii) roughly 757–782 kJ mol⁻¹.

EXPERIMENTAL

All mass spectra were determined using an AEI Kratos MS 902 double focusing mass spectrometer. Samples were admitted into the source through the all glass heated inlet system and ionization was effected by bombardment with electrons having a nominal energy of 70 eV. Typical source temperatures and pressures were 100 °C and 10^{-6} Torr, respectively.

The relative abundances of competing reactions were determined by the relative areas of the corresponding metastable peaks in the normal mass spectrum. In addition, the behaviour of ²H labelled analogues was checked, for ions decomposing in the first field free region, by increasing the accelerating voltage at constant electric and magnetic field strengths,¹¹ and by reducing the electric field at constant accelerating voltage and magnetic field strength.¹²

The average¹³ kinetic energy release measurements were obtained using the accelerating voltage scan technique¹¹ for ions fragmenting in the first field free region. No correction was applied for the width of the main beam; the peaks were recorded under identical operating conditions and the quoted results are the means of several scans.

All unlabelled compounds were synthesized by conventional procedures; the ²H labelled compounds were obtained by reduction of the corresponding urethanes using LiAlD_4 in diethyl ether or tetrahydrofuran:

$$RNHCO_2CH_2CH_3 \xrightarrow{LiAID_4} RNHCD_3$$

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REFERENCES

- L. Friedman and F. A. Long, J. Am. Chem. Soc. 75, 2832 (1952); see also D. H. Williams and I. Fleming, Spectroscopic Methods in Organic Chemistry, pp. 161–163. McGraw-Hill, New York (1973).
- 2. M. Karni and A. Mandelbaum, Org. Mass Spectrom. 15, 53 (1980).

3. H. M. Rosenstock, V. H. Dibeler and F. N. Harlee, J. Chem. Phys. 40, 591 (1964).

- 4. R. D. Bowen, D. H. Williams and H. Schwarz, Angew. Chem. Int. Ed. Engl. 18, 451 (1979).
- 5. B. J. Stapleton, R. D. Bowen and D. H. Williams, unpublished results.
- 6. N. A. Uccella, I. Howe and D. H. Williams, J. Chem. Soc. B. 1933 (1971).
- F. P. Lossing, Can. J. Chem. 49, 357 (1971).
 H. M. Rosenstock, K. Draxl, B. W. Steiner and J. T. Herron, J. Phys. Chem. Ref. Data, Suppl. 1, 6 (1977).
 R. D. Bowen and D. H. Williams, J. Chem. Soc., Perkin Trans. 2 1064 (1974).
- 10. R. D. Bowen and D. H. Williams, Org. Mass Spectrom. 12, 475 (1977).
- 11. K. R. Jennings, J. Chem. Phys. 43, 4176 (1965).
- 12. F. W. McLafferty, J. Okamoto, H. Tsuyama, Y. Nakajima, T. Noda and F. W. Major, Org. Mass Spectrom. 2, 751 (1969).
 13. D. T. Terwilliger, J. H. Beynon and R. G. Cooks, Proc. R.
- Soc. London Ser. A 341, 135 (1974).

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