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Short Communication

ON THE MICROSCOPIC REVERSIBILITY OF UNIMOLECULAR ETHYLENE LOSS FROM GASEOUS $C_5H_9^+$. ADDITION OF ALLYL CATIONS TO ETHYLENE IN THE GAS PHASE

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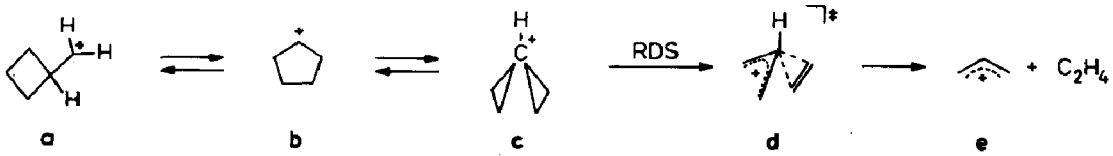
Recently [1], we provided experimental as well as theoretical evidence that unimolecular loss of C_2H_4 from $C_5H_9^+$ ions, generated in the gas phase from various precursors, is best described by the reaction outlined in Scheme 1,



which was found to represent the minimal energy requirement path. Ions, such as **a** and **b** prior to dissociation rearrange to the pyramidal cation **c** [2] whose electronic reorganisation leads, in a rate-determining step, to a partially ring-opened cyclopropyl cation, **d**, "solvated" by interaction with the departing C_2H_4 neutral. Transition state **d** eventually collapses to the allyl cation, **e**, and free ethylene. The intermediacy of **c** and analogues thereof [3] explains, among other features, why $C_5H_9^+$ and $C_6H_{11}^+$ ions prior to dissociation undergo complete positional loss of carbon and hydrogen atom identity.

Whereas most of the problems related to the chemistry of $C_5H_9^+$ and homologous ions are now well understood [1–3], it was not possible to provide clear evidence as to whether the reverse process takes place, i.e.

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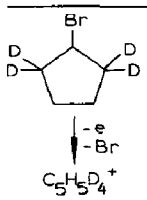
addition of ethylene to allyl-type ions

$$\mathbf{e} + C_2H_4 \rightarrow C_5H_9^+$$

and whether the $C_5H_9^+$ ions thus obtained have properties identical with species generated directly from an intact C_5H_9X precursor via dissociative ionization. This problem is not only of fundamental importance for probing the principle of microscopic reversibility in chemical dynamics; the addition of allyl-type ions to olefins is of great potential in synthetic organic chemistry [4]. Only a few reports appear to exist on the [3 + 2] cycloaddition reaction of allyl and methoxyallyl cations with olefins under ICR conditions in the gas phase [5]. Indeed, $C_5H_9^+$ ions are conveniently generated by the reaction of allyl cations **e** (derived from allyl bromide) with C_2H_4 in a conventional chemical ionization experiment. Similarly, the corresponding partially deuterium-labelled ions $C_5H_5D_4^+$ are formed by the ion/molecule reaction of allyl cations **e** with ethylene-d_4. Table 1 compares the unimolecular $C_2H_{4-x}D_x$ ($x = 0$–4) losses therefrom with the distribution obtained from the same $C_5H_5D_4^+$ precursor ions generated by dissociative ionization, i.e. loss of $Br^{\cdot}$ from [2,2,5,5-D_4]-bromocyclopentane. (The distributions were obtained from metastable ion spectra run with a VG Micromass ZAB-2F mass spectrometer.) It is seen that both routes yield an almost identical distribution of the $C_2H_{4-x}D_x$ species, which fits well with that calculated for a complete loss of positional identity (scrambling) of all nine hydrogen/deuterium atoms. We believe that this result is best explained in terms of the intermediacy of **b** ions, which are known to undergo rapid [1,2]-hydrogen migration [6]. Note, that the [3 + 2] cycloaddition of $\mathbf{e} + C_2H_4$ to form **b** directly is symmetry forbidden [7] and that the minimal energy requirement

TABLE 1

Unimolecular ethylene elimination from $C_5H_5D_4^+$ ions (m/z 73) [a]

	Precursor for $C_5H_5D_4^+$		Calculated distribution for $C_2H_{4-x}D_x$ elimination assuming complete loss of positional identity of H/D
		$C_2D_4 + C_3H_5^+$ ↓ $C_5H_5D_4^+$	
C_2H_4	4.4	4.1	3.9
C_2H_3D	33.5	33.1	31.8
$C_2H_2D_2$	47.2	47.3	47.6
C_2HD_3	14.2	14.8	15.9
C_2D_4	0.7	0.7	0.8

[a] Intensities are expressed in %. $\Sigma_{C_2H_{4-x}D_x} = 100\%$.

path to generate (collision stabilized) $C_5H_9^+$ adducts must proceed via transition state **d** [1a] from which eventually, via **c**, the cyclopentyl cation **b** may be formed.

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REFERENCES

1 (a) W. Franke, H. Schwarz, H. Thies, J. Chandrasekhar, P.v.R. Schleyer, W.J. Hehre, M. Saunders and G. Walker, Angew. Chem., 92 (1980) 488; Angew. Chem. Int. Ed. Engl., 19 (1980) 485. (b) W. Franke, H. Schwarz, H. Thies, J. Chandrasekhar, P.v.R. Schleyer, W.J. Hehre, M. Saunders and G. Walker, Chem. Ber., 114 (1981) 2808.
2 For recent reviews on pyramidal carbocations see: (a) H. Schwarz, Angew. Chem., 93 (1981) 1046; Angew. Chem. Int. Ed. Engl., 20 (1981) 991. (b) H. Schwarz, H. Thies and W. Franke, in M.A. Almoster Ferreira (Ed.), Ionic Processes in the Gas Phase, NATO ASI Series, C 118, Reidel, Amsterdam, 1984, p. 267.
3 W. Franke, G. Frenking, H. Schwarz and R. Wolfschütz, Chem. Ber., 114 (1981) 3878.
4 (a) H. Klein and H. Mayr, Angew. Chem., 93 (1981) 1069; Angew. Chem. Int. Ed. Engl., 21 (1981) 1027. (b) H. Klein, A. Erbe and H. Mayr, Angew. Chem., 94 (1982) 63. (c) H. Klein, G. Freyberger and H. Mayr, Angew. Chem., 95 (1983) 62. (d) H.M.R. Hoffmann, Angew. Chem., 96 (1984) 29.
5 (a) T.O. Tiernan and J.H. Futrell, J. Phys. Chem., 72 (1968) 3080. (b) P.G. Miasek and A.G. Harrison, J. Am. Chem. Soc., 97 (1975) 714. (c) R. Houriet and J.H. Futrell, Adv. Mass Spectrom., 7 (1977) 335. (d) M.W.E.W. van Tilborg, R. van Doorn and N.M.M. Nibbering, Org. Mass Spectrom., 15 (1980) 152.
6 (a) G.A. Olah and J. Lukas, J. Am. Chem. Soc., 90 (1968) 933. (b) G.A. Olah and A.M. White, J. Am. Chem. Soc., 91 (1969) 3954. (c) M.S. Shaw, R. Westwood and D.H. Williams, J. Chem. Soc. B, (1970) 1773. (d) K.B. Tomer, J. Turk and R.H. Shapiro, Org. Mass Spectrom., 6 (1972) 235.
7 R.B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry, Academic Press, New York, 1970.