

Gas Phase Isomerization of Pentyl Cations

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The isomerization of alkyl cations, both in solution and in the gas phase, is a well known phenomenon¹⁾. In this paper the results of a detailed study of the isomerizations of pentyl cations are presented.

The $C_5H_{11}^+$ ions were generated from isomeric pentyl bromides, pentenes, pentanols, and pentyl benzenes by EI and CI, respectively. The $C_5H_{11}^+$ ions fragment spontaneously only by loss of C_2H_4 independently of the structure of the precursor and the mode of generation. Although the CA spectra (Fig. 1, ZAB-2F, 2. FFR, He) do show some differences, these are clearly not related to the structure of the precursor. These differences are only observed for the intensity of elimination of C_2H_4 . In the CA spectra of $C_5H_{11}^+$ ions generated by CI, the loss of C_2H_4 is influenced to a large extent by the pressure of the CI reactant gas (Fig. 2). These results indicate a fast isomerization of all $C_5H_{11}^+$ ions to the most stable tertiary pentyl cation.

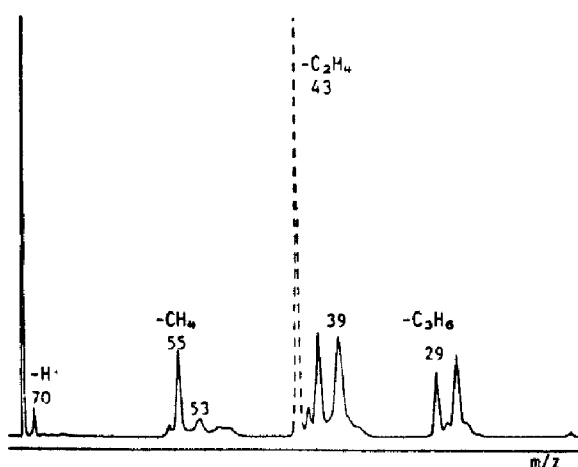


Fig. 1 CA spectrum $C_5H_{11}^+$ from 2-bromopentane/EI

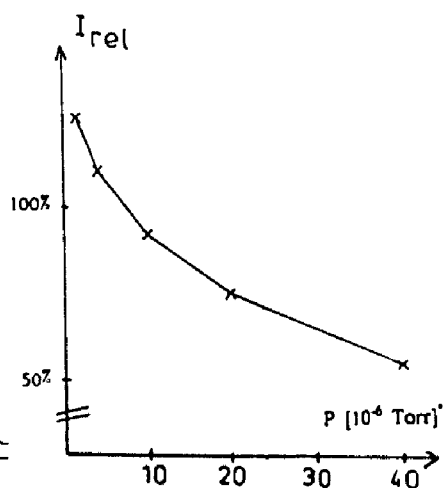
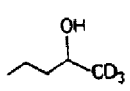
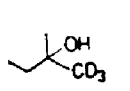
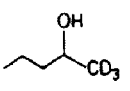
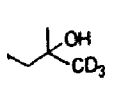


Fig. 2 Ethylene elimination in the CA spectrum $C_5H_{11}^+$ from 2-pentanol/CI(CH_4)

* measured at the ion source pump

This isomerization was studied further with the aid of precursors specifically labelled with D and ^{13}C . The results show that pentyl cations with sufficient internal energy for spontaneous elimination of C_2H_4 isomerize by complete scrambling of all H and C atoms. In contrast to metastable pentyl cations the label distribution of stable pentyl cations sampled by CA is non-statistical. The ratio of methane isotopomers eliminated from pentyl cations labelled with CD_3 and $^{13}\text{CH}_3$, respectively, indicates that the H and C atoms of the methyl groups are exchanged only partially in the stable ions. The extent to which the terminal H and C atoms are exchanged depends on both the structure of the precursor and the mode of ion generation (Table 1). For pentyl cations generated by CI, an influence of the CI reactant gas pressure is also observed: the exchange of terminal H and C atoms decreases with increasing gas pressure.

 Table 1. Partial CA spectra of $\text{C}_5\text{H}_8\text{D}_3^+$ ions

Compound:						
Ionisation:	CI(CH_4)		CI(<i>i</i> - C_4H_{10})		stat.:	prevailing loss of
m/z						
59	4.2	6.5	6.3	7.6	2.9	CH_3
58	22.9	25.8	26.4	26.5	18.5	CH_4
57	26.0	17.3	16.7	13.6	35.2	CH_3D
56	14.6	12.9	13.2	11.4	17.9	CH_2D_2
55	11.5	16.1	16.4	18.9	6.3	CHD_3
50-54	20.8	21.4	20.9	22.0	19.2	

The isomerization and the exchange of atoms is governed by the internal energy of the pentyl cations. Tertiary ions of low internal energies rearrange only by an interchange of the intact three methyl groups. At higher internal energies, an exchange of hydrogen atoms at the different positions is observed together with the isomerization of the different pentyl cation structures. A complete scrambling of all C and H atoms occurs at still higher internal energies.

In conclusion, our results show that the exchange of C and H atoms in pentyl cations is a function of their internal energy, which is determined by the structure of the precursor and the conditions during the ionization process.

In addition to these results we have studied the isomerization of pentyl cations by ICR experiments. The CA spectra of (labelled) pentyl cations measured by ICR show some remarkable differences to those obtained with the ZAB-2F:

- 1) Elimination of methane is not observed under all conditions.
- 2) Deuterium labelled pentyl cations loose ethylene with a statistical distribution of the label, indicating a complete scrambling of all H and D atoms in stable pentyl cations at long lifetimes typical for ICR experiments.