The Isomerisation of Hydrocarbon Ions, V[1]
Isomeric Pentylbenzenes and their $[M-CH_3]^+$ Fragments

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In contrast to the corresponding butyl ions the $[M-CH_3]^+$ ions from isomeric pentylbenzenes do not isomerise completely to a mixture of interconverting structures prior to decomposition.

It has been shown by ^{13}C labelling[2], metastable ion characteristics[3] and collisional activation (CA spectra)[1,4] that non radicalic *aliphatic* hydrocarbon ions, such as alkyl ions, initially differing in the branching of their carbon skeleton rearrange completely or to a large extent to a common structure or a mixture of interconverting structures prior to decomposition indicating that in these relatively stable even electron ions the lowest threshold for decomposition is higher than the threshold for interconversion (isomerisation) between the various isomeric structures. The tendency for isomerisation is, however, considerably reduced if a heteroatom or a heteroatom containing group is linked to the carbon chain[5] suggesting that the predominant localisation of the charge at the heteroatom increases the threshold for isomerisation relative to those for decomposition. In this study the influence of a phenylring on the isomerisation of alkyl ions is investigated.

For this purpose the CA spectra of both the molecular ions of isomeric pentylbenzenes and their even electron $[C_{10}H_{13}]^+$ fragments were compared. The identity of the CA spectra of the various isomeric ions is used as criterion for complete isomerisation to interconverting structures and collision induced decomposition through identical transition states.

The CA spectra of the molecular ions of four isomeric pentylbenzenes differ, as expected, considerably both in the types and relative abundances of their collision induced fragments (Table I), demonstrating that they *retain* their structural identity before decomposition. Loss of a methyl radical leads to even electron $[C_{10}H_{13}]^+$ fragments[6] which represent phenyl substituted butyl ions. As for butyl ions almost complete isomerisation (*i.e.* identical metastable ion abundances[3a] and CA

Table I*. Collisional activation spectra of the molecular ions of isomeric pentylbenzenes.

m/e	*sec-*	*tert-*	*n-*	*iso-*
	Pentylbenzene			
27	0.03	0.02	0.08	0.04
29	0.02	0.03	0.2	0.07
39	0.1	0.1	0.4	0.2
41	0.1	0.3	0.5	0.4
43	0.1	0.1	0.2	0.3
51	0.3	0.2	0.5	0.3
55	0.2	0.2	0.3	–
57	–	–	0.3	0.8
63	0.4	–	–	–
65	0.5	0.4	1.7	1.3
71	–	0.2	–	–
77	3.4	1.5	–	1.7
78	–	–	2.7	–
91	7.3	7.4	39	42
92	–	–	39	47
105	79	2.7	7.1	4.1
115	–	–	–	0.8
116	–	–	1.8	–
117	2.1	–	–	–
119	3.0	84	2.6	–
126	0.3	0.3	–	–
131	0.6	0.9	–	0.9
133	2.9	2.8	3.5	–

* CA spectra taken at 11 eV (nominal) were identical (within the reproducibility) with those at 70 eV.

Table II*. Collisional activation spectra of the $[M-CH_3]^+$ ions of isomeric pentylbenzenes.

m/e	*sec-*	*tert-*	*n-*	*iso-*
	Pentylbenzene			
27	0.04	0.08	0.2	0.07
29	0.04	0.1	0.07	0.05
39	0.3	0.4	0.7	0.6
41	0.1	0.2	0.7	0.7
51	0.5	0.8	1.1	1.1
53	0.2	0.5	1.0	0.9
55	0.5	2.4	1.9	1.4
63	0.7	0.7	1.4	1.2
64	–	–	–	1.4
65	1.0	1.1	2.3	1.7
67	–	–	2.6	0.6
77	1.3	3.1	4.7	3.2
78	–	–	–	2.3
79	–	–	3.5	–
91	80	67	41	52
103	–	3.3	–	–
104	3.3	–	–	–
105	–	6.3	16	12
116	4.0	5.2	9.7	7.5
117	8.4	8.7	15	13

* CA spectra taken at 13 eV (nominal) showed only minor differences to those at 70 eV.

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spectra[4a] as well as randomization of the carbon atoms[3a]) has been observed a similar behaviour might be expected for these even electron $C_{10}H_{13}^+$ ions. Table II, however, demonstrates that the $C_{10}H_{13}^+$ fragments give *distinct* CA spectra (even if the differences are less pronounced as for the molecular ions) suggesting that (if at all) only partial interconversion between isomeric ions can have occured prior to collision induced fragmentation.

This conclusion is supported by ^{13}C labelling data obtained for metastable and collision induced fragments from *n*-pentyl-benzene-δ-^{13}C. Table III reveals that the loss of C_2H_4 and C_3H_6 from $[C_{10}H_{13}]^+$ neither proceeds *via* direct cleavage (mechanism α), nor after complete randomization of all side chain carbons (mechanism β) or all carbons (mechanism γ). The data may be interpreted as *partial* randomization of the side chain atoms, but the pronounced differences between the values for loss of C_2H_4 and C_3H_6 suggest that not partial equilibration of the isomeric structures, but complicated skeleton rearrangements *during* decomposition explain the observed data. (The elucidation of the fragmentation mechanisms in alkylbenzene will be the subject of a separate study.)

Table III. Measured and calculated ratios for loss of $^{13}CCH_4/C_2H_4$ and $^{13}CC_2H_6/C_3H_6$ from the $[M-CH_3]^+$ ion of *n*-pentylbenzene-δ-^{13}C.

	Loss of $^{13}CCH_4/C_2H_4$	Loss of $^{13}CC_2H_6/C_3H_6$
Observed		
Metastable ions (2. field free region)	0.80 ± 0.04	0.59 ± 0.05
Collision induced dissociation	0.84 ± 0.02	0.63 ± 0.02
Calculated, assuming		
α direct cleavage	∞	∞
β side chain randomization	1.0	3.0
γ complete randomization	0.25	0.43

Summerizing the CA spectra in conjunction with ^{13}C labelling demonstrate that in contrast to butyl ions the corresponding phenyl-substituted butyl ions show (if at all) only partial equilibration between the various isomeric structures. The incomplete isomerisation can be explained either by an increase of the isomerisation barrier or by the presence of decomposition channels with lower activation energy than in the corresponding butyl ions. The process of lowest activation energy of these $C_{10}H_{13}^+$ ions is the formation of $C_7H_7^+$ ions by loss of C_3H_6 (formally α-cleavage). The threshold for this secondary decomposition, as determined by appearance potential measurements, ranges from 0.3 to 0.9 eV (Table IV). Thus, the lowest decomposition thresholds of these $C_{10}H_{13}^+$ ions are on the average *lower* than those of the corresponding butyl ions (ranging from 0.5–1.9 eV)[7]. Hence, the reduced tendency for isomerisation of these phenyl-substituted butyl ions (as compared to unsubstituted butyl ions) results at least in part from the presence of decomposition channels with low activation energy. In addition, the substitution of a hydrogen in a butyl ion by a phenyl ring may cause an increase of the isomerisation barrier, which cannot be determined directly.

Table IV*. Activation energy for loss of C_3H_6 from the $[M-CH_3]^+$ ion generated from isomeric pentylbenzenes.

Compound	ΔAP^* (eV)
n-Pentylbenzene	0.5 ± 0.2
iso-Pentylbenzene	0.3 ± 0.2
sec-Pentylbenzene	0.8 ± 0.2
tert-Pentylbenzene	0.9 ± 0.2

* ΔAP = appearance potential difference between $C_{10}H_{13}^+$ (direct peak) and $C_7H_7^+$ (metastable peak); semilogarithmic plot. These values contain an unknown contribution from the kinetic shift.

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