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THE INFLUENCE OF CHARGE LOCALIZATION ON THE ISOMERISATION OF ORGANIC IONS

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Abstract—Collisional Activation Spectra demonstrate that gaseous n- and iso-pentyl ions isomerise completely to a common structure prior to decomposition while no or only partial isomerisation is found with the analogous heteroatom containing fragments, n- and iso-$C_5H_{11}X^+$ ($X = -\overset{+}{C}\equiv O$, $-\overset{+}{O}=CH_2$, $-\overset{+}{N}H=CH_2$), suggesting that the predominant localization of the charge at the heteroatom reduces the tendency for isomerisation.

INTRODUCTION

Isomerisation of gaseous ions *prior to decomposition* is often observed in organic mass spectrometry.[1] For ion structure determination a better understanding of these internal rearrangements is desirable. Isomerisation of an ion A^+ prior to a given decomposition process can occur if the potential barrier for isomerisation, E_i, is lower than that for decomposition, $E_{0_{A^+}}$ (Fig. 1).

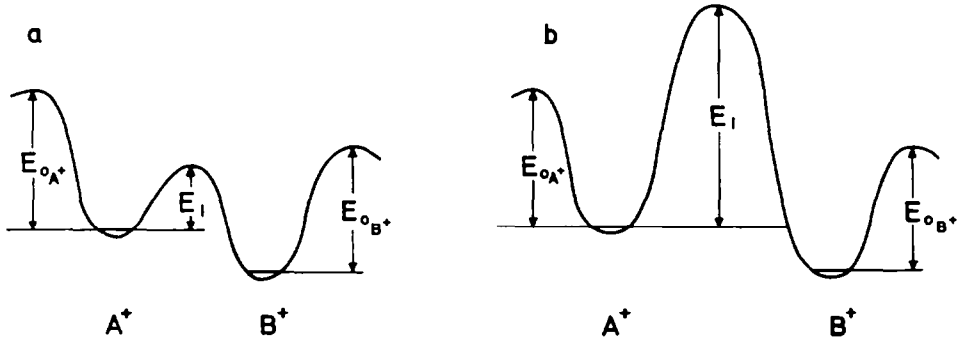

Fig. 1. Schematic potential diagram describing the isomerisation of an ion A^+ to B^+ (E_i = potential barrier for isomerisation, E_0 = activation energy of a given decomposition process). If $E_i < E_{0_{A^+}}$ isomerisation of A^+ to B^+ will occur, if $E_i \gg E_{0_{A^+}}$ no isomerisation will be observed (isomerisation is in principle possible at high excitation energies, but here decomposition will be much faster than isomerisation).

In recent years the structure of a large variety of *decomposing* ions has been studied using isotopic labelling, metastable ion characteristics, ion kinetic energy (IKE) and collisional activation (CA) spectra.[2] From these results one can generalize that isomeric aliphatic hydrocarbon fragments† isomerise completely or almost completely to common intermediates prior to decomposition[3] while heteroatom containing fragments in most cases retain their structural identity.[4] It has been concluded that the isomerisation reactions in such heteroatom containing fragments are less prevalent because of the low activation energies for decomposition.[4d]

This study aims to investigate in more detail the influence of a heteroatom on the isomerisation of a carbon skeleton. For this purpose the CA spectra of n- and iso-pentyl ions, on the one hand, and analogous heteroatom containing fragments of the general formula $[n\text{-}C_5H_{11}X]^+$ and $[iso\text{-}C_5H_{11}X]^+$ ($X = -\overset{+}{C}\equiv O$, $-\overset{+}{O}=CH_2$, $-\overset{+}{N}H=CH_2$), on the other hand, are compared. CA spectra have shown to be especially suited for fragment ion structure determination.[4b] The identity of CA spectra is used as criterion for identical structures and vice versa.

Since previous work[3d] demonstrated that n-pentyl- and iso-pentyl ions with a life time of $\sim 10^{-5}$ sec are completely isomerised prior to further decomposition the investigation of the corresponding heteroatom containing species is of interest in order to study whether the isomerisation of the carbon skeleton is influenced by the presence of a heteroatom. This question could be relevant in view of the recently revived discussion on the concept of charge localization as driving force for mass spectrometric reactions.[6]

RESULTS AND DISCUSSION

N- and iso-pentyl ions and their heteroatom containing analogues were generated by i- and α-cleavage from molecular ions of the general type $(n\text{-}C_5H_{11})_2Y^{+\cdot}$ and $(iso\text{-}C_5H_{11})_2Y^{+\cdot}$ (Y = CO, O, NH) as depicted in Scheme 1. The CA spectra of these 12 ions are contrasted in Table 1. Within the reproducibility identical spectra are obtained for all pentyl ions indicating that these ions have completely or almost completely isomerised prior to decomposition. However, considerable differences are observed with the isomeric $[C_5H_{11}\overset{+}{C}O]$ ions demonstrating that no isomerisation can have occurred at least prior to

†The situation is more complex with aromatic hydrocarbon ions where isomeric fragments with distinct structures have been found in several instances.[5]

$$[(n\text{-}C_5H_{11})_2CO]^{+\cdot} \xrightarrow{i} [n\text{-}C_5H_{11}]^+$$
$$\xrightarrow{\alpha} [n\text{-}C_5H_{11}CO]^+$$
$$[(iso\text{-}C_5H_{11})_2CO]^{+\cdot} \xrightarrow{i} [iso\text{-}C_5H_{11}]^+$$
$$\xrightarrow{\alpha} [iso\text{-}C_5H_{11}CO]^+$$
$$[(n\text{-}C_5H_{11})_2O]^{+\cdot} \xrightarrow{i} [n\text{-}C_5H_{11}]^+$$
$$\xrightarrow{\alpha} [n\text{-}C_5H_{11}OCH_2]^+$$
$$[(iso\text{-}C_5H_{11})_2O]^{+\cdot} \xrightarrow{i} [iso\text{-}C_5H_{11}]^+$$
$$\xrightarrow{\alpha} [iso\text{-}C_5H_{11}OCH_2]^+$$
$$[(n\text{-}C_5H_{11})_2NH]^{+\cdot} \xrightarrow{i} [n\text{-}C_5H_{11}]^+$$
$$\xrightarrow{\alpha} [n\text{-}C_5H_{11}\overset{+}{N}HCH_2]$$
$$[(iso\text{-}C_5H_{11})_2NH]^{+\cdot} \xrightarrow{i} [iso\text{-}C_5H_{11}]^+$$
$$\xrightarrow{\alpha} [iso\text{-}C_5H_{11}\overset{+}{N}HCH_2]$$

Scheme 1.

†A scrutiny of the previously published results reveals some further examples where isomeric heteroatom containing ions differing only in the branching of the carbon skeleton showed distinct structures. Thus no isomerisation was observed between the immonium ions of leucine and isoleucine containing peptides[8], $(CH_2)_3C{=}\overset{+}{X}$ and $CH_3CH_2CH{=}\overset{+}{X}$ (X = OH, NH_2).[4c,4e]

H_2O and CO loss. The differences in the relative abundances of the isomeric $[C_5H_{11}\overset{+}{O}CH_2]$ and $[C_5H_{11}\overset{+}{N}HCH_2]$ ions are less pronounced, but still so distinct that (if at all) only partial isomerisation can have occurred prior to decomposition. Lowering the electron energy to 12–14 eV (nominal) does not affect the relative abundance except for the fragments with lowest activation energy (recognizable by an abundant metastable ion) which decrease slightly. This demonstrates that the observed differences in abundance do not reflect differences in internal energy, but differences in structure. Thus, although the isomeric pentyl ions and the analogous heteroatom containing isomeric ions differ only in the same alkyl chain branching, isomerisation of the carbon skeleton is strongly reduced by the presence of a heteroatom.†

Two explanations are conceivable: (a) the heteroatom containing fragment may decompose through additional channels with higher rate constants (lower activation energy) so that $k_0 > k_i$ as $E_0 < E_i$ (Fig. 1). (b) The preponderant localization of the charge at the heteroatom leads to an increase of the potential barrier for isomerisation, E_i.

In order to distinguish between these two possibilities the appearance potential difference (ΔAP) between the primary fragment (using the normal peak) and the secondary decomposition process of lowest activation energy (using the metastable peak) has been determined for each ion in Scheme 1. As result of both the possible presence of a competitive and kinetic shift (especially

Table 1. Collisional activation spectra of n- and iso-$C_5H_{11}^+$ and n- and iso-$C_5H_{11}X^+$ ions (X = CO, OCH_2, $NHCH_2$)[a,b]

	Di-n-pentyl-ketone	Di-iso-pentyl-ketone		Di-n-pentyl-ether	Di-iso-pentyl-ether		Di-n-pentyl-amine	Di-iso-pentyl-amine
m/e	$[n\text{-}C_5H_{11}]^+$	$[iso\text{-}C_5H_{11}]^+$	m/e	$[n\text{-}C_5H_{11}]^+$	$[iso\text{-}C_5H_{11}]^+$	m/e	$[n\text{-}C_5H_{11}]^+$	$[iso\text{-}C_5H_{11}]^+$
15	0·3	0·3	15	0·2	0·2	15	0·3	0·3
27	5·4	4·8	27	4·7	4·5	27	4·9	4·6
29	4·3	4·1	29	4·9	4·6	29	5·0	4·7
39	6·6	6·2	39	7·4	6·9	39	6·4	6·6
41	9·5	9·1	41	11	10	41	10	10
43	59	61	43	56	59	43	61	60
51	1·7	1·5	51	1·5	1·5	51	1·2	1·3
53	3·3	3·2	53	2·9	2·9	53	2·8	2·7
55	10	9	55	11	11	55	8·9	9·7
m/e	$[n\text{-}C_5H_{11}CO]^+$	$[iso\text{-}C_5H_{11}CO]^+$	m/e	$[n\text{-}C_5H_{11}OCH_2]^+$	$[iso\text{-}C_5H_{11}OCH_2]^+$	m/e	$[n\text{-}C_5H_{11}NHCH_2]^+$	$[iso\text{-}C_5H_{11}NHCH_2]^+$
15	0·09	0·06	15	0·09	0·2	15	0·2	0·2
27	2·9	1·5	27	1·0	1·0	18	0·02	0·03
29	3·1	1·3	29	1·2	1·2	28	3·7	2·8
39	3·5	2·2	33	—	0·3	29	5·4	5·4
41	7·4	4·0	39	1·5	1·6	30	8·5	4·4
43	20	9·7	41	3·9	3·8	39	3·0	2·4
53	—	1·0	43	6·3	5·4	41	9·9	8·2
55	6·7	3·5	45	4·0	7·8	43	17	<7 [c]
57	2·3	1·5	55	1·5	1·3	44	37	64
69	—	1·4	59	3·6	8·5	56	4·7	5·6
71	49	8·1	69	49	54	70	4·7	1·7
81	4·9	66	71	27	13	71	4·9	2·4
			83	0·6	—	84	1·9	2·7
			85	0·6	2·0			

[a] Abundances relative to the sum all fragments.

[b] Spectra at low electron energy (12–14 eV nominal) are identical with 70 eV spectra except for the fragment of lowest activation energy the abundance of which is slightly reduced (by a factor of up to 1·15).

[c] Poorly resolved.

Table 2. Appearance potential differences between primary fragment and secondary fragment of lowest activation energy[a]

Compound	Initial Structure of Primary Fragment (m/e)	Secondary Decomposition Process	ΔAP (eV)[a]
Di-n-pentylketone	$[n\text{-}C_5H_{11}]^+$ (71)	71→43 ($-C_2H_4$)	0·7 ± 0·15
	$[n\text{-}C_5H_{11}CO]^+$ (99)	99→71 (−CO)	0·8 ± 0·15
Di-iso-pentylketone	$[iso\text{-}C_5H_{11}]^+$ (71)	71→43 ($-C_2H_4$)	0·8 ± 0·15
	$[iso\text{-}C_5H_{11}CO]^+$ (99)	99→81 ($-H_2O$)	0·4 ± 0·15
Di-n-pentylether	$[n\text{-}C_5H_{11}]^+$ (71)	71→43 ($-C_2H_4$)	1·0 ± 0·15
	$[n\text{-}C_5H_{11}OCH_2]^+$ (101)	101→69 ($-CH_3OH$)	0·3 ± 0·15
Di-iso-pentylether	$[iso\text{-}C_5H_{11}]^+$ (71)	71→43 ($-C_2H_4$)	1·0 ± 0·15
	$[iso\text{-}C_5H_{11}OCH_2]^+$ (101)	101→69 ($-CH_3OH$)	0·1 ± 0·15
Di-n-pentylamin	$[n\text{-}C_5H_{11}]^+$ (71)	71→43 ($-C_2H_4$)	1·2 ± 0·15
	$[n\text{-}C_5H_{11}NHCH_2]^+$ (100)	100→44 ($-C_4H_8$)	1·6 ± 0·15
Di-iso-pentylamin	$[iso\text{-}C_5H_{11}]^+$ (71)	71→43 ($-C_2H_4$)	1·2 ± 0·15
	$[iso\text{-}C_5H_{11}NHCH_2]^+$ (100)	100→44 ($-C_4H_8$)	1·4 ± 0·15

[a] ΔAP = appearance potential difference between primary fragment (normal peak) and secondary fragment (metastable peak). For further details see: Experimental Section.

with the normal peak) ΔAP corresponds only roughly to the activation energy of the secondary decomposition.

The ΔAp values, summarized in Table 2, show a non-uniform behaviour. While in three instances ΔAP is larger for the heteroatom containing fragment than for the corresponding pentyl ions the opposite situation is encountered with the remaining three ion pairs. Even if one keeps in mind the above mentioned sources of errors† this result still indicates that the potential barrier for the decomposition, E_0, is not always lower when a heteroatom is linked to the carbon skeleton. Thus the reduced tendency for isomerisation is, in general, not caused by the presence of additional decomposition processes with higher rate constants (lower activation energy) but by a decrease of the rate constant for isomerisation as result of a *higher potential barrier for isomerisation* resulting from the predominant localization of the charge at the heteroatom.

EXPERIMENTAL

CA spectra were measured on a self constructed double focussing mass spectrometer with reversed geometry (magnetic sector preceding electrostatic sector). Primary ions were produced in an EI source (electron energy: 70 eV; electron beam 20 μA, kinetic energy of the ions: 3 kV, source temperature: 250°C, gas inlet temp: 120°). For collisional activation helium was introduced via a variable leak valve into a collision chamber placed between magnetic and electrostatic sector. The leak rate was increased until the precursor ion intensity was reduced to 1/3 of its original value due to scattering and decomposition. After adjusting the magnet to pass the desired fragment the CA spectrum of this fragment was obtained by scanning the electrostatic sector potential.

All data are the means of at least two measurements (reproducibility about ± 10%). The ΔAP values were determined by appearance potential measurements of the precursor (normal peak) using the semilog-plot method and taking the voltage at which the abundance is 1% of its value at 50 eV. Values at 0·1% were either identical or slightly larger (up to 0·05 eV) than the 1% values (i.e. the semilog plots showed almost parallel curves) with the exception of the $C_5H_{11}^+$ ion from diisopentylamine where the 0·1% value was larger by 0·15 eV. The AP measurements were repeated on a second instrument under similar conditions leading to deviations of 0·1 eV in two instances, but smaller than 0·05 eV in all other cases. The pressure dependence of the metastable peaks revealed no collision induced contributions. Commercial samples (99%) were used without further purification.

†As rather different fragmentation processes are compared the kinetic shift may vary sizably. Thus the ΔAP values for the $C_5H_{11}^+$ ions from the three pairs of isomers differ considerably although the CA spectra point at common structures. As in some instances the pentyl ions are only formed via a secondary decomposition the observed differences in the ΔAP values may also result from a kinetic shift due to the partitioning of the excess internal energy.[9]

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