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STEREOELECTRONIC CONTROL OF ION FRAGMENTATIONS: LOSS OF HYDROGEN FROM CYCLIC ETHERS DURING ELECTRON IMPACT MASS SPECTROMETRY

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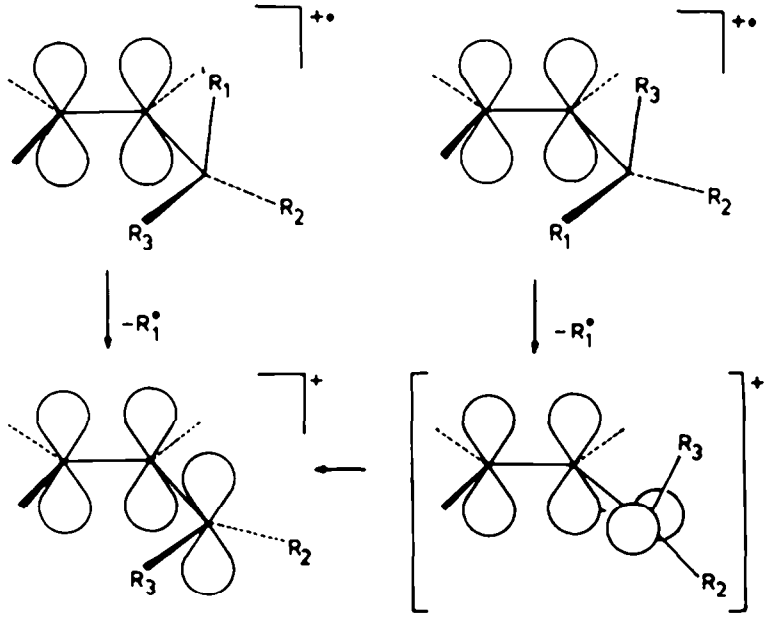
Abstract—Electron impact spectra of isomeric 7-oxabicyclo[4.3.0]nonanes differ in the relative abundance of $(M-H)^+$ ions. The critical energy of the angular hydrogen loss from the trans-annulated isomer **1** is lower by 9–10 kcal mol^{-1} than that of the cis-isomer **2**, due to stereoelectronic assistance of the neighbouring oxygen p_z orbital in the cleavage of the $C_{(6)}$–H bond in $\mathbf{1}^+$. High kinetic energy released during the hydrogen loss from $\mathbf{2}^+$, $\langle T \rangle = 7.5$ kcal mol^{-1}, is consistent with non-relaxed geometry of the resulting $(M-H)^+$ ion. Isomeric 2-oxabicyclo[4.4.0]decanes show analogous although smaller differences than **1** and **2**. Photoelectron, electron impact, metastable and collision induced decomposition mass spectra are reported.

Decomposition rates of organic compounds often depend on the geometric arrangement of a bond to be cleaved and a neighbouring orbital of *n* or π type. This stereoelectronic effect[1,2] has been encountered with species of a different nature such as cations,[3-6] anions,[7-11] carbenes,[12,13] and radicals.[14-21] The orbital interaction can either increase or decrease the reaction rate, depending on population of bonding and antibonding states in the product.[7-10] Stereoelectronic control is limited to cases in which the configuration of the transition state resembles that of the product.[22] Such a situation is common with simple bond cleavages occuring in decompositions of organic ions in the gas phase as examined by mass spectrometry. Let us consider a fragmentation of two isomeric ions (Scheme 1): In the first case, the loss of R^1 is favoured by the bonding π-allylic interaction leading to a configuration which corresponds to the ground state of the product, while the second isomer would yield a high energy biradical ion. If the latter reactant ion cannot assume relaxed geometry in the transition state due to bridging or other steric restrictions, the loss of R^1 will require a considerable critical (activation) energy corresponding to a high internal energy product ion. Differences in critical energies are very sensitively reflected by the relative abundance of daughter ions in the mass spectra of isomers. For example, the rates of abstraction of diastereotopic



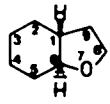
Scheme 1.

allylic hydrogen atoms from ionized 1,4-dihydroxy-$\Delta^{6,7}$-octalins differ by a factor of thirteen in favour of the pseudoaxial hydrogen.[23]

The non-bonding orbital on a heteroatom can also control the reactivity of an adjacent center as documented by numerous examples from the chemistry in solution.[14-21] By contrast, only one case of the stereoelectronic control exerted by a heteroatom on ion fragmentation has been recognized by Longevialle and Astier[24] in the mass spectra of isomeric 3-dimethylamino-3-methylcholestanes. More examples could be found in the literature; before presenting some we will analyze conditions that are to be fulfilled in order to distinguish the stereoelectronic effect from other intervening factors.

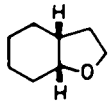
Reactive (unstable) gaseous ions which have a high internal energy decompose rapidly, the lifetime being less than 1 μs. Owing to the energy excess, unstable conformations such as the boat form of cyclohexane are easily adopted and populated, as documented by mechanisms of water elimination from cyclic alcohols.[27] On the contrary, in order to observe stereoelectronic effects it is necessary that the relative orientation of the directing orbital and the splitting bond be fixed. This is best achieved in cyclic systems in which the conformational motion is restricted by annulation or bulky substituents.[28-30] If the heteroatom is a part of the ring, bonds linking axial substituents will be nearly coplanar with the controlling non-bonding orbital,[31-33] while with equatorial substituents the corresponding dihedral angle will be 60–90° depending on the heteroatom hybridization. Hence, a preferential loss of an axial group can be anticipated in analogy with solution chemistry.[14,15] However, due to steric interactions, axial isomers are usually less stable than their equatorial counterparts so that a slight preference for the loss of the axial group is observed even in the absence of the controlling orbital.[34-36] Although this thermochemical effect gives rise only to small differences in the mass spectra of isomers,[34-36] it works in the same direction as does the stereoelectronic effect and, hence, both kinds of the reactivity control are not easily distinguished. For example, in the mass spectra of substituted perhydroquinolines the molecular ion of the axial isomer loses the $C_{(2)}$ methyl group more readily than does the equatorial isomer.[25] Zaikin *et al.*[25,26] explained this finding on thermochemical grounds, although the same stereospecificity could be anticipated by considering stereoelectronic (i.e. kinetic) control.

In order to separate and then investigate the stereoelectronic effect in mass spectra, we have chosen as a model reaction the loss of hydrogen from ionized 7-oxabicyclo-[4.3.0]nonanes **1** and **2** and 2-oxabicyclo[4.4.0]decanes **3** and **4**.[37] In part we were prompted by recent papers on radicals generated from similar systems in solution.[14,15] Moreover, due to the small size of the hydrogen atom axial and equatorial C H bonds should differ very little in synclinal steric interactions, so that the thermochemical effect should be avoided. The bicyclic systems also make it possible to adjust the geometrical arrangement of the angular C–H bond with respect to the oxygen p_z orbital. In the first pair of isomers, the dihedral angle between the p_z orbital and the adjacent bonds (ϑ) is either frozen (trans-isomer **1**) or can be varied by conformational excitation of the carbocyclic ring (cis-isomer **2**). With the second pair, ϑ can be changed either by flipping the heterocyclic ring (**3**) or by independent motion of both rings (**4**). In order to elucidate fragmentation mechanisms we prepared labelled compounds **1a–1d**, **2a–2e**, **3a–3c** and **4a–4f**.[37]



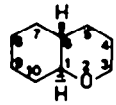
1

1a: 1-$^2H_1$
1b: 6-$^2H_1$
1c: 8,8-$^2H_2$
1d: 9,9-$^2H_2$



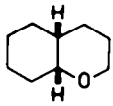
2

2a: 1-$^2H_1$
2b: 6-$^2H_1$
2c: 8,8-$^2H_2$
2d: 9,9-$^2H_2$
2e: 5-$^2H_1$



3

3a: 1-$^2H_1$
3b: 3,3-$^2H_2$
3c: 6-$^2H_1$



4

4a: 1-$^2H_1$
4b: 3,3-$^2H_2$
4c: 6-$^2H_1$
4d: 4,4-$^2H_2$
4e: 5,5-$^2H_2$
4f: 10-$^2H_1$

RESULTS AND DISCUSSION

Following ionization, **1**$^+$ and **2**$^+$ decompose by several fragmentation paths (Scheme 2). Cleavage of the C-5–C-6 bond, followed by transfer of the angular hydrogen from C-1 and subsequent loss of $C_3H_7^{\cdot}$ produces ion **a**, $C_5H_7O^+$. As corroborated by the spectra of the labelled compounds, more than 95% of the C-1 hydrogen is incorporated into the C_3H_7 neutral fragment (compounds **1a**, **2a**), while hydrogens from C-6, C-8 and C-9 remain completely in **a** (**1b–1d**, **2b–2d**). Further characterization of **a** was provided by the collision induced decomposition (CID) spectra[38] (Table 1). In accordance with the labelling data, the CID spectra of **a** prepared from **1** and **2** are identical indicating that ions of the same structure are formed from both annulation isomers. By comparison, the CID spectrum of **a** differs from those of four $C_5H_7O^+$ isomers prepared from various precursors,[39] suggesting that stable **a** have not undergone profound skeletal rearrangements.

The loss of hydrogen from **1**$^+$ and **2**$^+$ giving rise to ions **b**, $C_8H_{13}O^+$, also displays high specificity as confirmed by the mass spectra of **1b** (95% $(M-^2H)^+$, 5% $(M\ H)^+$) and **2b** (98% $(M-^2H)^+$, 2% $(M-H)^+$). There is a visible isotope effect if losing deuterium instead of hydrogen, $k_H/k_D = 1.7$ and 1.6 for **1b** and **2b**, respectively. Again, the CID spectra of **b** prepared from **1** and **2** were identical (Table 1), confirming the structural identity inferred from the labelling experiments. Other fragmentations of **1**$^+$, **2**$^+$, **a** and **b**

Table 1. The CID spectra of $C_5H_7O^+$ (**a**) and $C_8H_{11}O^+$ (**b**)

	Relative intensity[a]			
	a		b	
m/z	1	2	1	2
109	-	-	1.2	1.2
107	-	-	(6.5)	(6.3)
97	-	-	(6.6)	(8.4)
96	-	-	7.6	7.0
95	-	-	1.7	2
91	-	-	1.7	2
83	-	-	6.1	6.5
82	5.7	6.5	-	-
81	7.1	6.8	(16.6)	(26.6)
79	-	-	3.9	4
77	-	-	2.4	3
69	-	-	2.7	3
68	-	-	2.4	2
67	0.3	-	(5.1)	(6)
66	-	-	2	2
65	0.9	1.1	2.5	2
63	-	-	1.2	1
60	-	-	0.8	:
57	-	-	1.7	2
55	(19.2)	(22.1)	25.5	27
54	4.1	4.5	-	-
53	11.4	11	5.1	5
51	5.8	7.1	-	-
50	5.6	5.6	-	-
43	1.4	1.6	3.4	3
41	-	-	8.8	8
39	13	14.2	7.8	8
38	4	4	-	-
37	2.8	2.5	-	-
31	0.7	0.4	-	-
29	11.4	11.9	2.5	2
28	4.1	3.3	-	-
27	16.6	15.4	4.6	5
26	4.1	4.1	-	-
25	0.9	-	-	-

[a]Related to the sum of ion intensities. The values in parentheses were excluded from the summation because of contribution of metastable ions

(Scheme 2) were deduced from unimolecular decompositions of metastable precursors, CID spectra and electron impact (EI) mass spectra of labelled derivatives.

Molecular ions of **3** and **4** behave analogously, as do $\mathbf{1}^+$ and $\mathbf{2}^+$. The main fragmentation gives rise to ions $C_6H_9O^+$ formation of which was largely elucidated by means of deuterium labelling. Thus, the $C_3H_5^+$ radical eliminated contains the C-8–C-9–C-10 segment and one hydrogen atom transferred from C-6. The specificity of the latter transfer exceeded 95% (compounds **3c** and **4c**). The loss of hydrogen from $\mathbf{3}^+$ and $\mathbf{4}^+$ is less specific than with $\mathbf{1}^+$ and $\mathbf{2}^+$, nevertheless, the elimination of the angular C-1 hydrogen still predominates as evidenced by the spectra of **3a** (89% $(M-^2H)^+$, 11% $(M\ H)^+$) and **4a** (91% $(M\ ^2H)^+$, 9% $(M\ H)^+$). The 75 eV EI mass spectra of **1**–**4** are shown in Figs. 1 and 2. Despite a general similarity, the spectra of the annulation isomers differ significantly in the relative intensity of M^+, **a** and **b** (related to the sum of all ion intensities above *m/z* 38, Figs. 1 and 2). Since only stable ions (lifetime $\geq 15\ \mu s$ in this case) are detected in conventional mass spectra, the relative abundance reflects the rates of both ion formation and decomposition. Thus even if **b** were formed easier from one isomer, the relative

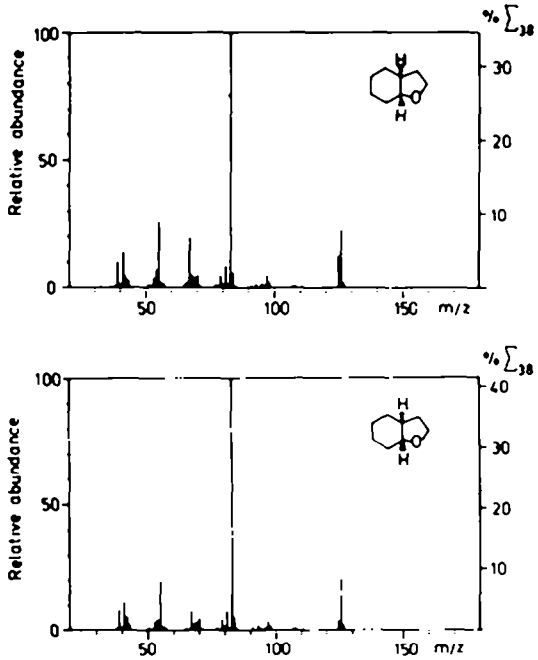
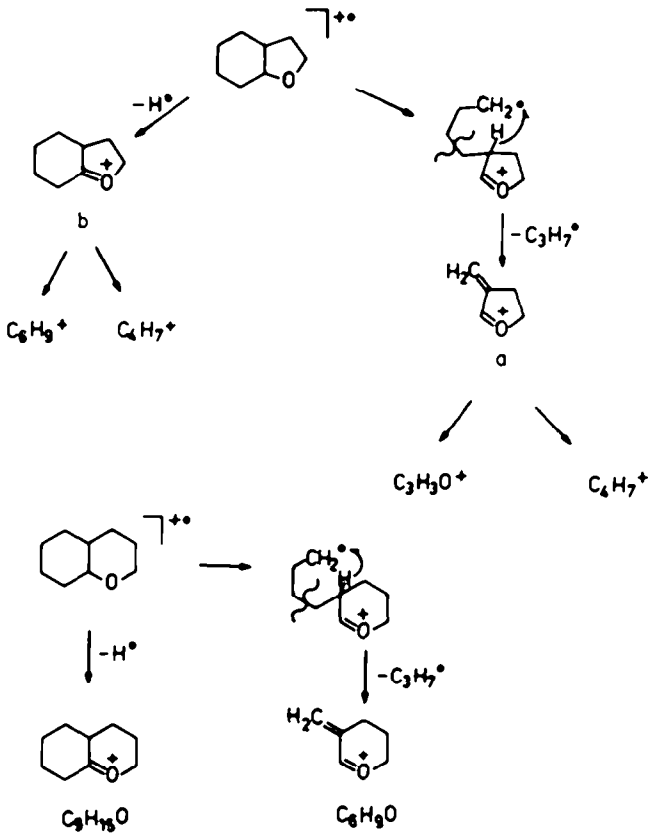


Fig. 1. The 75 eV mass spectra of **1** and **2**.



Scheme 2.

abundance of these stable ions could have been counterbalanced by a further decomposition in favour of the other isomer provided the isomers had differed in the internal energy gained upon ionization. The internal energy distribution is inaccessible from EI mass spectra, however, it can be very roughly estimated from the photoelectron spectra.[40] Figure 3 shows that the photoelectron spectra of **1** and **2** are nearly superimposable, giving the vertical ionization energy IE = 9.24 ± 0.04 eV for both isomers. By analogy,[40] the population of excited states in $\mathbf{1}^+$ and $\mathbf{2}^+$ could be also similar. Secondary decompositions can be effectively supressed by lowering the electron energy. Figure 4 shows the dependence of the relative abundances [M⁺], [**a**] and [**b**] (related to the sum of ion intensities) on the ionizing energy. Although [M⁺] and [**a**] from **1** and **2** differ at 75 eV, the differences decrease at low energies and vanish at the threshold. The appearance energy of **a** is the same within experimental error for both isomers: AE(a) = 10.56 and 10.57 eV for **1** and **2**, respectively. Formation of **a** from metastable molecular ions is accompanied by a small kinetic energy release, $\langle T \rangle$ = 0.6 (n = 1.9) and 0.7 kcal mol^{-1} (n = 2.1)[43] for **1** and **2**, respectively. As the formation of **a** is a multi-step process, it appears that the rupture of the C-5–C-6 bond is not the rate determining step which would explain the identical critical energies and kinetic energy release. The difference in [M⁺] and [**a**] at 75 eV is due to the competing loss of hydrogen which is more facile in $\mathbf{1}^+$ than in $\mathbf{2}^+$. In contrast, the difference in [**b**] (if expressed as a ratio $[b]_{trans}/[b]_{cis}$) increases steeply near the threshold and also the appearance energies considerably differ: AE(*b*) = 10.11 and 10.52 eV for **1** and **2**, respectively. These data made it possible to draw an approximate

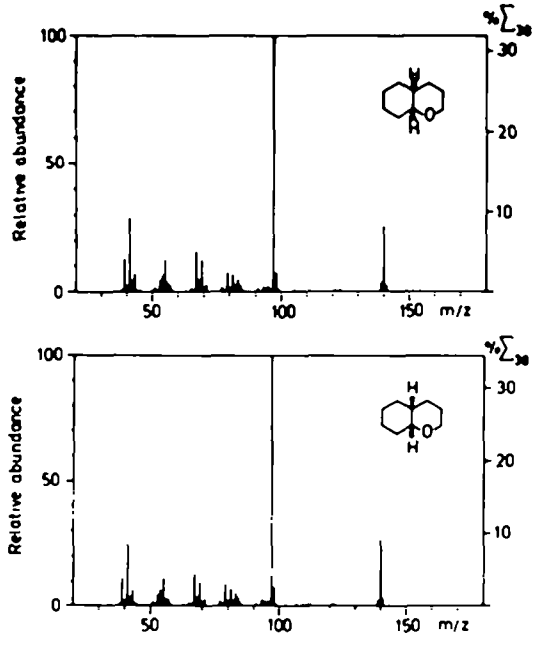


Fig. 2. The 75 eV mass spectra of **3** and **4**.

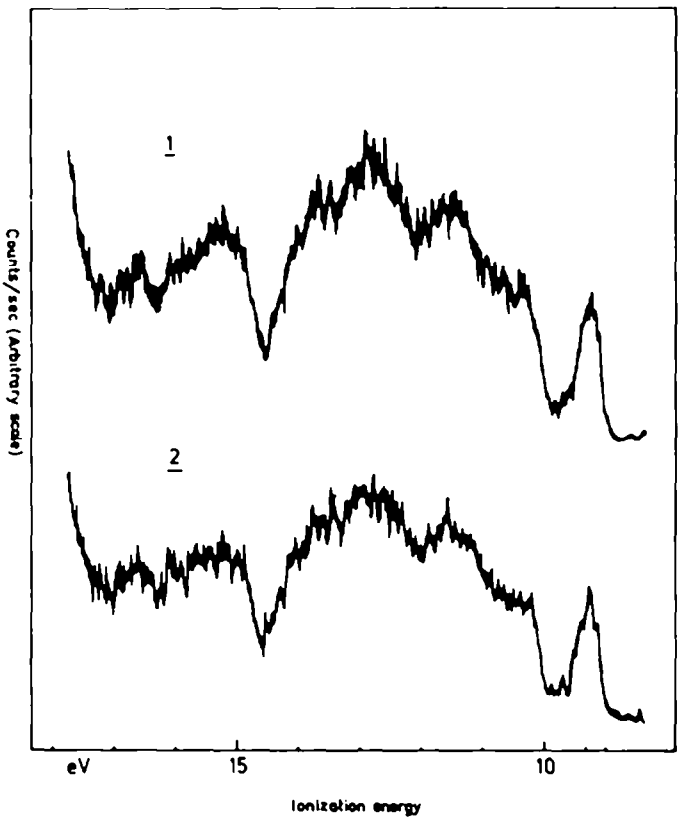


Fig. 3. The photoelectron spectra of 1 and 2.

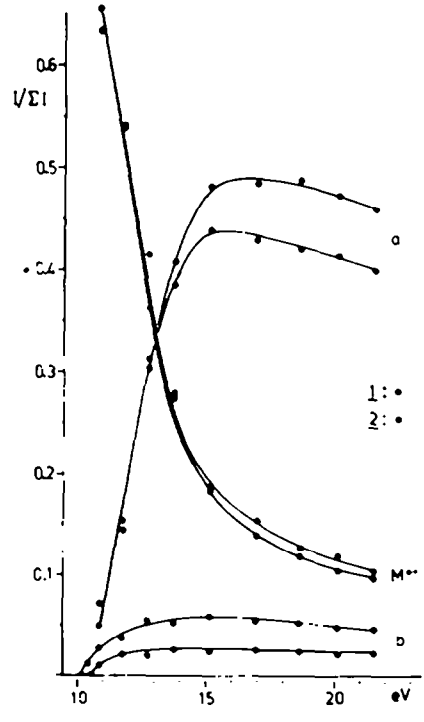


Fig. 4. The relative intensity vs electron energy plots of [M·⁺], [a] and [b] in the mass spectra of 1 and 2.

energy diagram depicting the formation of M·⁺, **a** and **b** from **1** and **2** (Fig. 5)). Although experimental heats of formation of **1** and **2** are unknown, we estimate that they differ by less than 1 kcal mol $^{-1}$. This estimate stems from ΔH_f of isomeric hydrindanes[41] (ΔH_f(trans-ΔH_f(cis) = $-$ 1 kcal mol $^{-1}$) and also from lower A-values of alkoxy groups when compared with n-alkyl groups having the same number of heavy atoms.[42] Hence, substitution of a CH_2 segment in hydrindanes by the ether oxygen should not increase the difference in ΔH_f between the annulation isomers. Since the ionization energies of **1** and **2** are equal, ΔH_f of **1**·⁺ and **2**·⁺ should be very similar, too. With respect to the difference in AE(**b**) this means that the critical energies for the loss of the C-6 hydrogen do differ by 9–10 kcal mol $^{-1}$ (Fig. 5), despite of the structural identity of ions **b** formed. This suggests that **b** originating from **2**·⁺ are not produced at the thermochemical threshold, so there must be a barrier for the reverse reaction. Accordingly, the kinetic energy released during the hydrogen loss from metastable **2**·⁺ ($\langle T \rangle$ = 7.5 kcal mol $^{-1}$, n = 2.05) is higher than with **1**·⁺ ($\langle T \rangle$ = 5.4 kcal mol $^{-1}$, n = 2.10).

Due to the apparent mechanistic simplicity of the formation of **b** from both **1** and **2**, we exclude rearrangements taking place prior to the loss of hydrogen. Note also that the difference in $\langle T \rangle$ between isomers cannot be attributed to the centrifugal barrier.[44] The effect can be qualitatively explained by

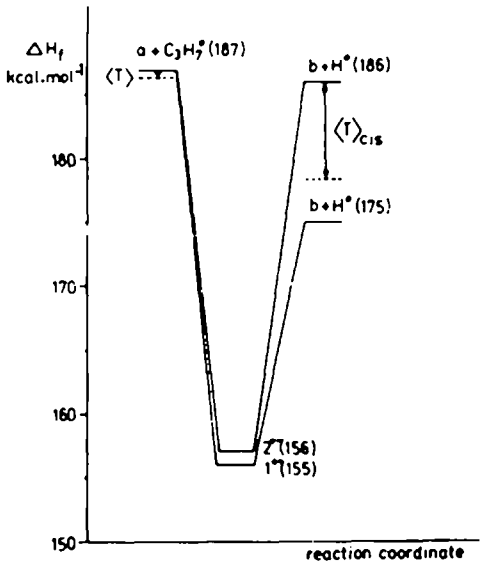


Fig. 5. The energy profile of formation of **a** and **b** from **1**⁺ and **2**⁺.

stereoelectronic control of the $C_{(6)}$–H bond dissociation exerted by the p_z orbital of the neighbouring oxygen atom. In the trans-isomer **1**, the dihedral angle ϑ between the $C_{(6)}$–H bond and the p_z orbital[31] varies within 15 30° depending on the conformation of the six-membered ring (an estimate from relaxed Dreiding models). Therefore, regardless of conformational excitation the geometrical arrangement of bonds in **1**⁺ favours the orbital interaction and, moreover, the ground state conformations of the reactant and product ion directly correlate (Fig. 6). On the other hand, in **2**⁺ ϑ can vary within 0–90° due to the flexibility of the cis-annulated skeleton. Of two possibly stable chair conformations, one (hereinafter denoted chair I) has the $C_{(6)}$–H bond oriented axially with respect to the cyclohexane ring, ϑ being about 15°, while the second form (chair II) has the $C_{(6)}$–H bond equatorial with ϑ close to 90° (Fig. 6). Thus the rupture of the latter bond may or may not be assisted by orbital interaction, depending on the actual molecular conformation. In solution the chair I conformation appears to be more stable[37] which is consistent with the difference in A-values of alkoxy and alkyl groups.[42] Following ionization, chair II can be stabilized by bonding interaction of the semioccupied p_z orbital with the $C_{(1)}$–$C_{(6)}$ and $C_{(5)}$–$C_{(6)}$ bonds, thus reversing the relative stability of both conformations.

In high energy **2**⁺, both chair I and II can be significantly populated because of a small energy difference in the ground state which would have a negligible impact on the density of states in decomposing ions. Despite that the critical energy of the hydrogen loss from **2**⁺ is higher than an estimated barrier to conformational inversion (10–12 kcal mol⁻¹),[45] the latter transformation is entropically more demanding so that it can contribute to the overall reaction rate. While in **1**⁺ all reactive molecular ions have a proper geometry favouring a facile hydrogen loss, a significant portion of **2**⁺ must either lose the angular hydrogen via an unfavourable transition state (chair II) or first isomerize to chair I in which the bond cleavage can be stereoelectronically assisted. As a result, the loss of hydrogen from **2**⁺ is less frequent than from **1**⁺, giving rise to the differences in the mass spectra (Fig. 1). At low internal energies the conformational inversion should be faster than the hydrogen loss and the fragmentation via chair I could become more important. Nevertheless, both the rapid decline of [**b**] at low internal energies and higher appearance energy show that the channel **2**⁺ (chair II)→**2**⁺(chair I)→**b** is more energy demanding than **1**⁺→**b**. This can be rationalized assuming that the ring system in stable **b** remains intact. Model geometries show that the stable (chair) conformation of **b** does not correlate with any low-energy conformation of **2**⁺. Therefore the rupture of the $C_{(6)}$–H bond produces the former ion in a non-relaxed, vibrationally excited state thus

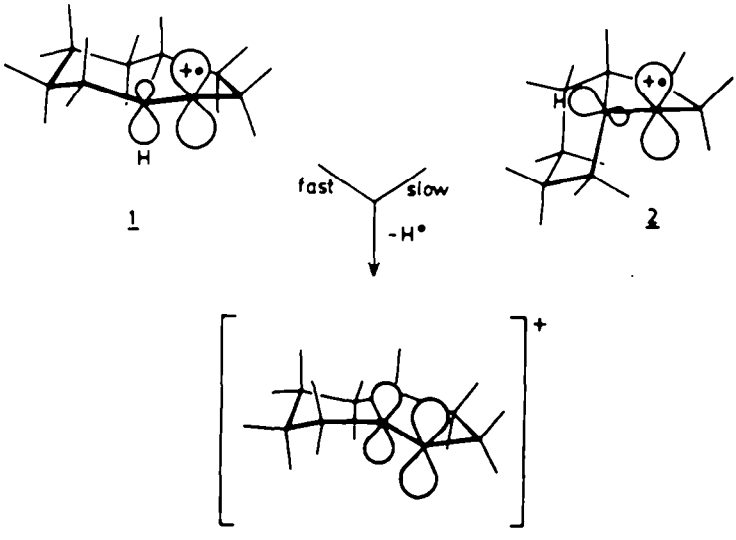


Fig. 6. The orbital interaction in **1**⁺, **2**⁺ and **b**.

increasing the critical energy above that corresponding to the thermochemical threshold (*vide supra*).

It should be mentioned that metastable $\mathbf{1}^{\ddagger}$ and $\mathbf{2}^{\ddagger}$ which decompose after $\sim 25\,\mu s$ give very similar relative abundance of **b** (Table 2). Since the CID spectra of stable, long lived $\mathbf{1}^{\ddagger}$ and $\mathbf{2}^{\ddagger}$ are also very similar (Table 2), it appears that the isomeric ions slowly interconvert to a common structure or a mixture thereof.

A difference in relative abundances of $(M-H)^{+}$ ions was also found in the mass spectra of **3** and **4** (Fig. 2). Although of a low intensity, $(M-H)^{+}$ ions from **3** are more abundant than those from **4**, the difference increasing at very low ionizing energies (Fig. 7). We explain this effect in the same way as with **1** and **2**. In **3**, the dihedral angle ϑ is $\sim 40°$ in the stable chair–chair conformation and changes within 0–40° by conformational motion of the heterocyclic ring. Thus the cleavage of the $C_{(1)}$-H bond in $\mathbf{3}^{\ddagger}$ is promoted by the oxygen p_z orbital though less efficiently than in $\mathbf{1}^{\ddagger}$ due to a larger ϑ. cis-Isomer **4** can adopt two chair-chair conformations (chair I and II; *vide supra*), ϑ being 40 and 90°, respectively. Inspection of models further reveals that a conformation of $\mathbf{3}^{\ddagger}$ in which ϑ is optimal (0°) directly correlates with the stable chair–half chair form of $(M-H)^{+}$. No such possibility exists in $\mathbf{4}^{\ddagger}$ in which conformations having favourable ϑ correlate with unstable boat-like forms of $(M-H)^{+}$.

The examples presented in this paper have shown that the stereoelectronic control is a common phenomenon in fragmentations of organic ions. Further studies exploring the scope, limitations and analytical applications of this effect are in progress in this laboratory.

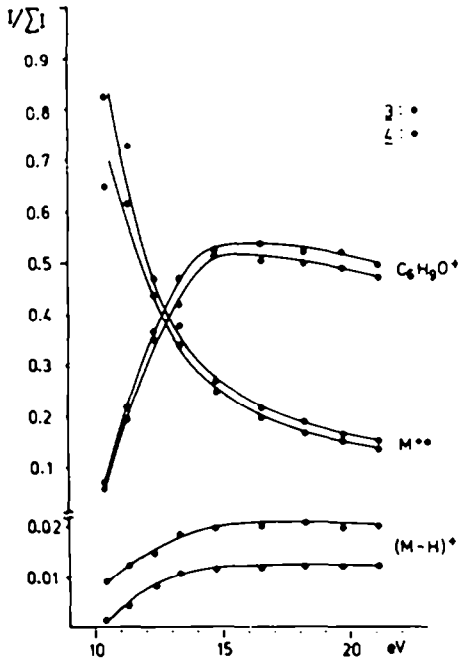


Fig. 7. The relative intensity vs electron energy plots of $[M^{\ddagger}]$, $[C_6H_9O^{+}]$ and $[M-H^{+}]$ in the mass spectra of **3** and **4**.

Table 2. The metastable and CID spectra of $\mathbf{1}^{\ddagger}$ and $\mathbf{2}^{\ddagger}$

	Relative intensity[a]			
	Metastable		Collision-induced	
m/z	1	2	1	2
125	33.6	33.2	(26.4)	(25.0)
111	5.3	4.2	(2.2)	(2.6)
108	7.9	7.9	(8.5)	(10.4)
98	14.7	14.3	(6.9)	(13.3)
97	11.8	11.0	(10.3)	(14.8)
96	-	-	2.6	4.3
95	-	-	4.5	2.7
93	-	-	2.6	3.4
91	-	-	-	1.9
83	22.6	24.5	(190.8)	(199.8)
81	0.8	1.6	8.5	7.7
79	-	-	5.5	9.7
77	-	-	2.1	4.1
70	3.5	2.8	(4.2)	(6.8)
69	-	-	5	-
68	-	-	3.2	-
67	-	-	5.3	6.0
65	-	-	2.4	1.9
57	-	-	2.1	3.6
55	-	-	14.3	11.1
53	-	-	5.3	6.5
51	-	-	2.6	1.9
43	-	-	4	3.1
41	-	-	9.8	9.9
39	-	-	8.5	10.4
29	-	-	4.5	5.1
27	-	-	5.5	6.3

[a]See the footnote to Table 1

EXPERIMENTAL

The 75 eV mass spectra were recorded on a JEOL JMS D-100 spectrometer. Samples were introduced via a heated inlet system at 60°, ion source conditions were: emmission current 300 μA, temperature 150°. Appearance energies were measured with 50 μA emmission current and the repeller voltage set to zero. The data were evaluated by the electron energy distribution difference method[46] using 50 mV steps and $b = 0.47$ which gave both linear portions of the $\Delta I(V)$ curves near thresholds and correct ionization energies for 1 and 2. Benzene (IE = 9.245 eV) was used as a calibrant. The photoelectron spectra were obtained on a VG Scientific UVG 3 spectrometer using xenone (IE = 12.13 eV) as a reference. The reported ionization energies are each an average of ten measurements. Unimolecular decompositions of metastable ions were recorded on the Cornell University tandem MS-MS instrument.[47] 9.9 keV ions decomposing between the first and second collimating lenses of the collision chamber (5th field free region of the Cornell instrument[47]) were monitored by scanning the electrostatic analyzer voltage. The pressure was 3.10^{-7} torr as measured directly in the collision chamber. The kinetic energy release data were obtained with narrow analyzer slits, giving the main beam halfwidth 0.6 V at 9.9 keV ($E/\Delta E = 800$). The halfwidths of metastable peaks were corrected for the energy spread in the main beam using the formula of Ottinger.[48] The CID spectra were recorded on the same instrument using helium as a collision gas and beam attenuation 25% of the original ion current. The reported spectra are each a computer-smoothed average of ten repetitive scans.

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