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Characterization of anomeric differences of ammonium-bound monomeric and dimeric complex ions of 1α- and 1β-azido-pentofuranosyl derivates by kinetic method

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Dedicated to Professor J.H. Beynon on the occasion of his 80th birthday for his huge contribution to mass spectrometry

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Abstract

Relative stabilities (ΔG^c) of ammonium-bound monomers and dimers of anomeric β-D-pentofuranosyl 1α- and 1β-azide derivates are determinate using the kinetic method by measuring relative rates of competitive collision-induced dissociations of dimeric $[ANH_4B]^+$ and trimeric $[A_2NH_4B]^+$ or $[ANH_4B_2]^+$ cluster ions. Comparison between calculated ammonium affinities (AAs) and relative stabilities (ΔG^c) of ammonium-bound monomers shows qualitative correlations between both thermochemical quantities, but in two examples the activation barrier differences of competitive fragmentation channels cause a large disparity between both thermochemical data. Therefore, the most stable ammonium-bound monomers of the anomeric 1α- and 1β-2,3,5-tri-*O*-benzyl-β-D-arabino-pento-furanosyl azides possess the lowest ammonium affinities and the highest relative stabilities. Two different relative stabilities measured for the same ammonium-bound homo- or hetero-dimers indicate dissimilar activated barriers of trimers transition states for dimer formations. The activated barriers of trimers depend on the relative stabilities of ammonium-bound monomer within the trimeric cluster ions.

Keywords: Electrospray ionization; Kinetic method; Ammonium-bound dimers and trimers; Ammonium affinities; CID-MIKE spectra; Anomeric pentofuranosyl azides

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1. Introduction

Electrospray [1,2] or fast atom bombardment ionization [3] of compounds from solutions or from liquid matrix usually produces more or less abundant cluster ions, which compose an ion solvated with one, two or more molecules. The stability of a positive charge cluster composed of a proton, a metal ion, an ammonium ion or various organic ions solvated with organic molecules, depends on the difference in Gibbs free energy (ΔG^c) of clustering reaction. The gas-phase thermochemical properties of various reactions of molecules and protons, such as proton affinity (PA), gas-phase basicity (GB), gas-phase acidity and the entropies of protonation were thoroughly investigated by mass spectrometry. Hunter et al. reported [4] proton affinities and related thermochemical data investigations on approximately 1700 molecules, radicals and atomic neutral species. Thermochemical data on clustering an ammonium ion with neutral molecules are less extensive [5–13] and to the best of our knowledge only two publications [5,6] on the ammonium affinities of the molecules (AA(M)) are available.

Cooks and coworkers [14–16] developed the kinetic method which has been often used for the determinations of molecular thermochemical values. In a tandem mass spectrometry experiment the appropriate cluster ions can be isolated, internally excited and their competitive product-ions quantitatively measured [14]. The application of the kinetic method to the competitive dissociation of a proton bound dimer (reaction 1) gives the relative gas-phase basicity (ΔGB) of the molecules:

$$A–H^+–B \rightarrow AH^+ + B, \quad (k_A) \qquad (1a)$$

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$$A\text{–}H^+\text{–}B \rightarrow BH^+ + A, \quad (k_B) \tag{1b}$$

and

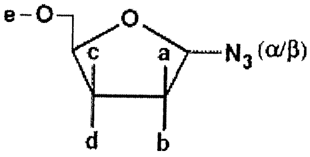
$$\ln\left(\frac{k_A}{k_B}\right) = \ln\left(\frac{[AH^+]}{[BH^+]}\right) = \frac{GB(A) - GB(B)}{RT} = \frac{\Delta GB(A,B)}{RT} \approx \frac{\Delta H}{RT} \approx \frac{\Delta PA(A,B)}{RT} \tag{2}$$

A and B are molecules, GB(A) and GB(B) are their gas-phase basicities, k_A and k_B are the rate constants of monomers formation and the values in square brackets indicate abundances of AH^+ and BH^+ fragment ions. R is a gas constant and T is defined as the effective temperature [16–18] which represents an average of an internal energy of reactive ions. The approximation $\Delta GB(A, B) \approx \Delta PA(A, B) = \Delta H(A, B)$ can be obtained by applying product-ion measurements of series of reference bases (B_i) of those that are chemically and structurally similar to measured compounds [14–17,19]. If this condition is not satisfied, the entropy change (ΔS) or the total entropy of reaction $\Delta(\Delta S)$ are not negligible and the kinetic method is actually measuring the gas-phase basicities rather than proton affinities [20].

Vekey and Czira [21,22] extended the kinetic method to determine molecular-pair gas-phase basicity (MPGB) by measuring CID products of proton-bound trimers of some amino acids by tandem mass spectrometry. They obtained the values of the gas-phase basicities of homo- and hetero-dimers of amino acids when they used a series of independent equations based on eight different ion abundance values. Some of these equations were used to calculate the effective temperature [21] of various reactive trimeric clusters.

Cooks and coworkers applied the kinetic method for the chiral recognition of amino acids and on chiral drugs [23,24] based on single-charge trimeric copper(II)-bound complexes. A complex of chiral reference compound and sample were generated by electrospray mass spectrometry and the kinetics of competitive CID fragmentations of trimeric Cu(II)-bound complexes provided relative Cu(II) affinities for homo-and hetero-chiral Cu(II)-bound dimeric cluster ions as indicators of chiral discrimination.

This paper reports the application of the kinetic method [21] to determine molecular-pair gas-phase relative stabilities (ΔG^c) of ammonium-bound dimers and monomers of anomeric pentofuranosyl azides (Scheme 1). Competitive dissociation of collision activated ammonium-bound dimers and trimers, i.e., with two and three molecules of 1α- or 1β-azido-pentofuranosyl derivatives, are bound to ammonium ion. The ammonium-bound monomer, homo-dimer and -trimer are obtained by electro spray ionization of methanol and ammonium acetate solution of one compound and homo and hetero-dimeric and trimeric ammonium clusters are detected using the solution of two compounds. The relative free energies of the formation of the ammonium-bound monomers and dimers are obtained from CID products of selected ammonium-bound hetero-dimeric and trimeric cluster ions. Selected measurements are compared with calculated ammonium affinities of these compounds by the semi-empirical molecular orbital method [25] (AM1).



Scheme 1.

Compounds:

1(α/β): a = c = d = H, b = e = $C_6H_5CO_2$
(2,5-di-*O*-benzoyl-3-deoxy-ribose)
2(α/β): a = c = H, b = d = e = $C_6H_5CO_2$
(2,3,5-tri-*O*-benzoyl-xylose)
3(α/β): b = d = H, a = c = e = $C_6H_5CO_2$
(2,3,5-tri-*O*-benzoyl-arabinose)
4(α/β): b = d = H, a = c = e = $C_6H_5CH_2O$
(2,3,5-tri-*O*-benzoyl-arabinose)
5(α/β): a = b= d = H, c = e = p-Cl-$C_6H_4CO_2$
(3,5-di-*O*-(*p*-chlorobenzoyl)-2-deoxy-ribose)
6(α/β): a = b= d = H, c = e = p-$CH_3C_6H_4CO_2$
(3,5-di-*O*-(*p*-methylbenzoyl)-2-deoxy-ribose)

2. Experimental

The syntheses of compounds 1–6 were described elsewhere [26,27]. All mass spectral measurements were performed on an AutoSpecQ mass spectrometer of EBEqQ configuration (Micromass, Manchester, UK). The ESI interface was maintained at 60 °C and a flow of warm N_2 was used as nebulizer (20 l/h, 6 bar) and bath gases (200 l/h) to control solvent declustering. A differential voltage of 40 V was maintained between the sampling and skimmer cones. Sample solutions (10^{-3} mol l^{-1}) were introduced into the ESI interface with a syringe pump at a flow rate 10 μl/min. CID-MIKE spectra [28] were obtained by introducing the collision gas into MIKE collision cell at a pressure sufficient to decrease the main beam of ions by 10%. Data of CID peak intensity ratio was averaged from 30 scans.

3. Results and discussion

3.1. ESI mass spectra

Electrospray mass spectra [1,2] (Fig. 1) of the solution of the individual compounds 1–6 contain peaks characteristic of the ammonium ion complex with one, two, three and four molecules of azidofuranosides. Besides peaks of monomer, homo-dimer, homo-trimer and homo-tetramer, the peak with smaller *m/z* corresponds to the $[M\text{–}N_3]^+$ fragment ion, namely the pentofuranosyl cation ($[S]^+$). Relative in-

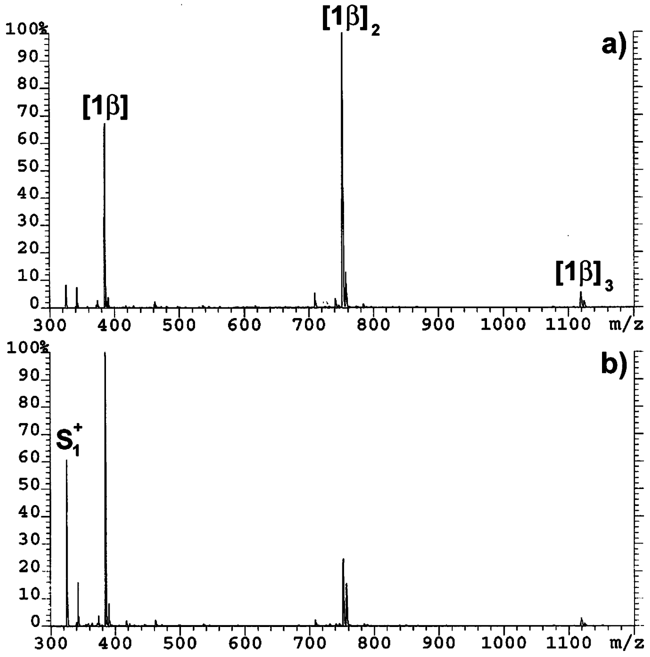


Fig. 1. ESI mass spectra of compound 1β applying different voltages between sampling and skimmer zone, Δ*V*: (a) 50 V and (b) 150 V.

tensities of peaks depend on the voltage difference applied between the sampling and skimmer zone of electrospray interface. At higher voltage difference (>100 V) abundance of hetero-dimers and -trimers becomes considerably smaller (Fig. 2). Likewise the MNH$_4^+$ peaks of the compounds lα and 1β (Fig. 2a and b) are nearly five times smaller while the S$_1^+$ fragment ion peaks become the most intensive peaks of ESI mass spectra. It was noted that the homo-dimers composing molecules with higher ammonium affinities (or higher relative free energies of clusters formation) are more stable than the homo-dimers of less reactive molecules.

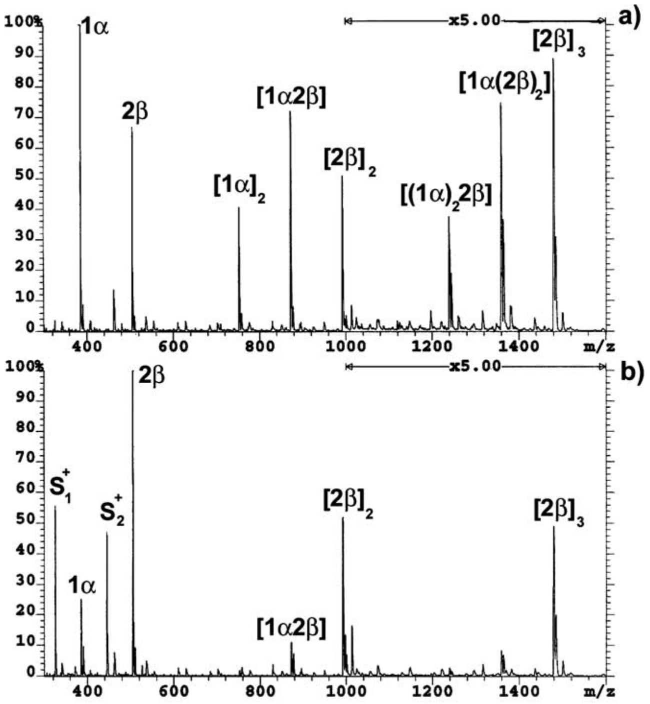


Fig. 2. ESI mass spectra of compounds lα and 2β; Δ*V*: (a) 50 V and (b) 150 V.

3.2. CID-MIKE spectra of ammonium-bound clusters

The metastable product ion peaks were two orders of magnitude less abundant than the CID-fragment. Therefore, the fragmentation of cluster ions was studied by the mass analyzed ion kinetic energy technique (MIKE) using the collisions of high kinetic energy (4 keV) ions with target gas molecules.

3.2.1. CID-MIKE spectra of collision activated MNH$_4^+$

Ammonium-bound monomers obtained in electrospray (ESI) or ammonia chemical ionization CI(NH$_3$) of compounds 1–6 [13] give the same product-ion peaks though they differ in relative peak intensities especially by loss of NH$_3$ from parent ions.

Thus, NH$_3$ loss from MNH$_4^+$ ions obtained by ESI is insignificant process (1–5% of all product ions) comparing to the ammonium-monomers formed in CI(NH$_3$) process where the [MNH$_4$–NH$_3$]$^+$ ions are formed in mono-molecular process [13] and they represent the most intensive peaks in MIKE spectra of MNH$_4^+$ ions. However, the basic peak in CID-MIKE spectra of the MNH$_4^+$ ions obtained by ESI or CI(NH$_3$) corresponds either to pentofuranosyl cation S$^+$($\equiv$[MNH$_4$–(NH$_3$ + HN$_3$)]$^+$) or to MH$^+$ and S$^+$ product ions, respectively.

3.2.2. CID-MIKE spectral data of ammonium-bound dimers

The required conditions and limits of the kinetic method [14–16], known in its application to competitive dissociation of proton bound-dimers in obtaining the thermochemical values are the same, and sometimes more rigorous for the cation [17] and especially ammonium-bound dimers and trimers. The kinetic method is usually applied to the loosely-bound clusters which should decompose to monomers without activation energy for reverse reaction. The structures of transition states are similar or easy inter convert to those of decomposition products. The overall entropy difference of products in measurements of proton affinity and gas-phase basicity by kinetic method may be suspended by using the "similar" references. The calibration of analyte with similar references gives also a factor *RT* which multiplied by logarithm of intensity ratio, evaluates the proton affinity difference.

The difference in proton affinities and gas-phase basicities [PA(M) − GB(M)] of a great number of compounds are about 30 kJ/mol and when a proton is stabilized in the molecule by intramolecular hydrogen bonds it is even higher for 15–30 kJ/mol [4].

The adoption of the kinetic method [14–16] to the competitive dissociation of ammonium-bound dimer of the compounds 1–6 (reactions 3 and 3a) gives the relative gas-phase stabilities (ΔG^{c}) (Eq. (4)) of ammonium-bound monomers:

$$[\mathrm{ANH_4B}]^+ \begin{array}{l} \rightarrow \mathrm{B} + \mathrm{ANH_4}^+ \\ \rightarrow \mathrm{A} + \mathrm{BNH_4}^+ \end{array} \tag{3}$$

$$\begin{aligned} &\mathrm{ANH_4}^+ \rightarrow \mathrm{S_A}^+ + (\mathrm{HN_3} + \mathrm{NH_3}), \\ &\mathrm{BNH_4}^+ \rightarrow \mathrm{S_B}^+ + (\mathrm{HN_3} + \mathrm{NH_3}) \end{aligned} \tag{3a}$$

and

$$\begin{aligned} \left(\frac{k_{\mathrm{A}}}{k_{\mathrm{B}}}\right) &= \ln\left(\frac{[\mathrm{ANH_4}^+] + [\mathrm{S_A}^+]}{[\mathrm{BNH_4}^+] + [\mathrm{S_B}^+]}\right) \\ &= \frac{[G^{\mathrm{c}}(\mathrm{A}) - G^{\mathrm{c}}(\mathrm{B})]}{RT} = \frac{\Delta G^{\mathrm{c}}(\mathrm{A,B})}{RT} \end{aligned} \tag{4}$$

G^{c}(A) and G^{c}(B) are free energies of dissociations (or stabilities) of ammonium-bound monomers to molecule and ammonium ion. G^{c} is equal to negative free energy of formation of monomer ($-\Delta_{\mathrm{f}}G$) and ΔG^{c}(A,B) is the difference of energies for the $\mathrm{ANH_4}^+$and $\mathrm{BNH_4}^+$ dissociation channels. The formalisms AA(M) and G^{c}(M) are adopted from proton-bond definitions, where the terms proton affinity [PA(M) → AA(M)] and gas basicity [GB(M) → G^{c}(M)] are well known [3,4]. The relationship between the difference of ammonium affinity (ΔAA) and stability (ΔG^{c}(A,B)) of ammonium monomers of compounds A and B in the reaction (3) is obtained by Eq. (5):

$$\begin{aligned} \Delta G^{\mathrm{c}}(\mathrm{A,B}) &= -\Delta H(\mathrm{A,B}) + T\Delta(\Delta S_{\mathrm{A}}(\mathrm{A,B})) \\ &= \Delta\mathrm{AA}(\mathrm{A,B}) + T\Delta(\Delta S_{\mathrm{A}}(\mathrm{A,B})) \end{aligned} \tag{5}$$

The corresponding entropy change can be expressed in terms of entropy change of the species involved in reaction 3: $\Delta(\Delta S(\mathrm{A,B})) = [S^0(\mathrm{ANH_4}^+) - S^0(\mathrm{A})] - [S^0(\mathrm{BNH_4}^+) - S^0(\mathrm{B})] = \Delta S_{\mathrm{A}}(\mathrm{A}) - \Delta S_{\mathrm{B}}(\mathrm{B})$. ΔS_{A}(A) and ΔS_{A}(B) are entropy changes of ammonium attachment process to A and B molecules. The difference of ΔG^{c}(A,B) and ΔAA(A,B) can be interpreted by term $T\Delta(\Delta S_{\mathrm{A}})$. Rearranging Eq. (5) gives

$$\Delta(\Delta S_{\mathrm{A}}(\mathrm{A,B})) = R\ln\left(\frac{k_{\mathrm{A}}}{k_{\mathrm{B}}}\right) - \frac{\Delta\mathrm{AA}(\mathrm{A,B})}{T} \tag{6}$$

Using similar references in ammonium-bound dimers means that ΔS_{A}(A) and ΔS_{B}(B) could be neglected or they are identical ($\Delta(\Delta S_{\mathrm{A}}(\mathrm{A,B})) = 0$).

These formalisms Eqs. (4)–(6) are valid for fragmentations of the dimers (or trimers) when the dissociation energy barrier of particular reaction channel is not higher than the free energy of stabilization (ΔG^{c}) of formed monomers (or dimers). This means that there is no activation energy for reverse reaction. At higher energy barriers the ΔG^{c} and the activation free energy ($\Delta G^{\#}$) of transition states are measured by the kinetic method. Differences in the entropy of activation was clearly demonstrated by Armentrout [17] for Li^+ affinities to alcohols and water.

The product ion intensity data obtained from CID-MIKE spectra of the ammonium-bound hetero-dimer cluster ions $[\mathrm{ANH_4B}]^+$ of the compounds 1–6 are shown in Table 1. The accuracy of intensity measurements is between 5 and 10% and it was controlled using the peak intensity ratios of all possibly dimeric pairs. We measured 22 of over 40 possible ratios to determinate 12 values of 12 compounds. The relative thermochemical properties of anomeric pairs and the pairs of the compounds 2 and 3 were measured indirectly by dimers $[\mathrm{ANH_4B}]^+$ where anomers A and B were of different molecular masses as it is shown in Table 1. Thus, lα and 1β compounds were measured with both anomers of 2, 3, 4, 5 and 6 or vice versa. However, the same molecular masses of all anomeric pairs and of the pairs of the compounds 2 and 3 prevent direct observation of their clusters stabilities.

Two examples in Fig. 3 show that the ammonium-bound hetero-dimers dissociate in both monomers (reaction 3) and to the furanosyl cations ($\mathrm{S}_i{}^+$) (reaction 3a). The loss of $\mathrm{NH_3}$ from dimer clusters or from monomers product ions was not noticed. The relative intensities of S^+ peaks in CID-MIKE spectra of ammonium-bound dimers are 40–60% of the $\mathrm{MNH_4}^+$ monomer peaks for the less stable monomer and 18–50% for more stable monomers (Table 1). The measurements of $\Delta G^{\mathrm{c}}_{\mathrm{rel}}$ of these compounds give adequately the same values for all pairs only when the intensities of both product ion peaks: $[\mathrm{ANH_4}^+] + [\mathrm{S_A}^+] = k_{\mathrm{A}}$ or $[\mathrm{BNH_4}^+] +$

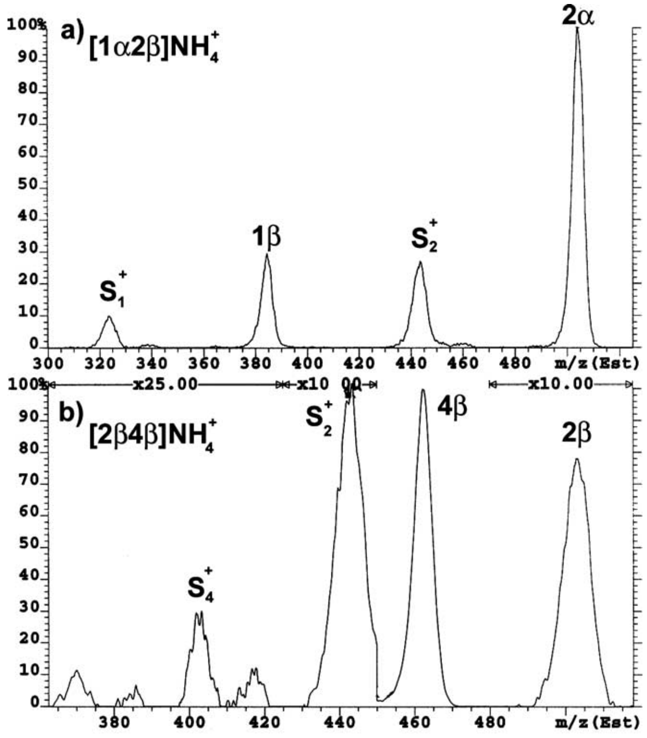


Fig. 3. CID-MIKE spectra of hetero-dimers: (a) $[1\beta\mathrm{NH_4}2\alpha]^+$ and $[2\beta\mathrm{NH_4}4\beta]^+$ ($\mathrm{S}_i{}^+$ furanosyl cation and 1β, 2β, etc. ammonium-bound monomers).

Table 1
Relative intensities and logarithm (ln) of their ratios of the competitive product ions of $[ANH_4B]^+$ hetero-dimers and $[A_2NH_4B]^+$ hetero-trimers

Dimers $[NH_4]^+$		Intensity of products monomers		$\ln(k_A/k_B)$[a]	$\ln(k_A/2k_B)$ trimers[b]	
A	B	[A] (S_i^+)[c]	[B] (S_i^+)[c]			
1α	2α	13 (5)	100 (23)	−2.0	−2.0	−1.8
1α	2β	9 (3)	100 (28)	−2.4	−2.5	−2.4
1β	2α	28 (7)	100 (27)	−1.3	−1.3	−1.1
1β	2β	16 (6)	100 (39)	−1.8	−1.8	−1.7
1α	3β	4.5 (1)	100 (20)	−3.1		
1β	3α	8.5 (3)	100 (15)	−2.5	−2.7	
1β	3β	9 (4)	100 (15)	−2.4		
1β	4α	14 (5)	100 (1)	−2.0		
1β	4β	6 (2)	100 (1)	−2.8		
1α	5α	100 (19)	39 (7)	0.9		
1α	5β	100 (15)	59 (13)	0.5		
1β	5β	100 (32)	25 (3)	1.4		
3α	4β	28 (9)	100 (2)	−1.3		
3β	4β	25 (8)	100 (1)	−1.4		
1β	6α	37 (13)	100 (19)	−1.0		
1β	6β	45 (20)	100 (25)	−0.6		

[a] $\ln(k_A/k_B) = \ln\{[ANH_4^+ + S_A^+]/[BNH_4^+ + S_B^+]\}$.
[b] These values are obtained from timers (see Table 4).
[c] Abundance of furanosyl fragment ion S_i^+) participating to monomer ion intensity.

$[S_B^+] = k_B$ are used in the rate constants. The participation of the fragment ion peaks S_A^+ or S_B^+ to the intensities of ANH_4^+ or BNH_4^+ monomeric peaks is shown in Table 1 in the round brackets. Values in the last two columns represent the natural logarithms of total product ion peak intensity ratio of monomers formed by decomposition of trimers (see next section).

The logarithms (ln) of relative peak intensity ratio are shown in Table 1 (column 5) and the relative values of $\Delta G^c(\mathrm{M}, 1\alpha)/T = \Delta G^c_{\mathrm{rel}}(\mathrm{M})/T = R\ln([k_M]/[k_{1\alpha}])$ of the compounds 1–6 are calculated in Table 2 (column 3) where the value of $G^c(1\alpha)/T$ is selected as zero (=0). The effective temperatures T of reactive dimers are not known, since these measurements cannot be calibrated by a series of compounds of known thermochemical data (G^c and AA) and results in Table 2, column 3 are given as $\Delta G^c_{\mathrm{rel}}(\mathrm{M})/T$. However, a compound like glucose (though its ammonium affinity and G^c are not known) forms dimer with 1α, while in the CID-MIKE spectrum of the $[(\mathrm{glucose})NH_4(1\alpha)]^+$ dimer, the competitive CID-product ion-peak $[(\mathrm{glucose})NH_4]^+$ is completely missed. The values of $\Delta G^c_{\mathrm{rel}}(\mathrm{M})$ are given in column 4 of Table 2 only to illustrate the order of magnitude. They were calculated assuming the $T = 500\,\mathrm{K}$. The temperature could be wrong for ±50%. However, more real background of assumed T is obtained with comparing literature data of proton-bound di- and trimers of amino acids ($T \approx 1000\,\mathrm{K}$) [21,22], and considering the proton affinities and gas basicities of amino acids, which are about six times higher than AA's and G^c of the compounds 1–6.

The data in Table 2 show the order of ammonium-bound monomer clusters stabilities: $5\alpha < 5\beta < 1\alpha < 6\beta < 1\beta < 6\alpha < 2\alpha < 2\beta < 3\beta < 3\alpha < 4\alpha < 4\beta$, which are

Table 2
Relative free energies ($\Delta G^c_{\mathrm{rel}}(\mathrm{M})/T$)[a] of ammonium-bound ion formation ($\Delta G(1\alpha)/T = 0.0$)[a] and relative ammonium affinities ΔAA(M) [AA(1α)≡0]of compounds 1–6

Compound M	$\ln(k_M/k_{1\alpha})$	$\Delta G^c_{\mathrm{rel}}(\mathrm{M})/T$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	$\Delta G^c_{\mathrm{rel}}(\mathrm{M})T = 500\,\mathrm{K}$ ($\mathrm{kJ\,mol^{-1}}$)	ΔAA(M) ($\mathrm{kJ\,mol^{-1}}$)
1α	0.0	0.0	0.0	0.0
1β	0.7	6.0	3	1
2α	2.0	17	8	4
2β	2.4	20	10	8
3α	3.3	27	14	11
3β	3.1	26	13	7
4α	4.0/2.6[b]	33/22	17/11	−7
4β	4.5/3.3[b]	37/27	19/14	−11
5α	−0.9	−7	−4	
5β	−0.5	−4	−2	
6α	1.7	14	7	

[a] Relative to 1α, i.e., $\Delta G(1\alpha)/RT = 0.0$.
[b] Values 4.0 and 4.5 is obtained from dimers with 3α, and 3β; 2.6 and 3.3 from 1α and 1β.

Table 3
Ammonium affinities of compounds 1–4

Compound	Ammonium affinity ($kJ\,mol^{-1}$)	
	α[a]	β[b]
1α	145 (137)[c]	139 (132)
1β	146 (142, 100)	146 (137, 125)
2α	134 (131, 128)	148 (133)
2β	153 (147, 145)	147 (145, 143)
3α	145 (144)	156 (149, 142)
3β	149 (147)	152 (149, 143)
4α	107 (100)	138 (129)
4β	115 (107)	135 (126, 125)

[a] The side (α or β) of ammonium attached to the pentofuranosyl azide molecule.

[b] The side (α or β) of ammonium attached to the pentofuranosyl azide molecule.

[c] AA values of less stable monomer.

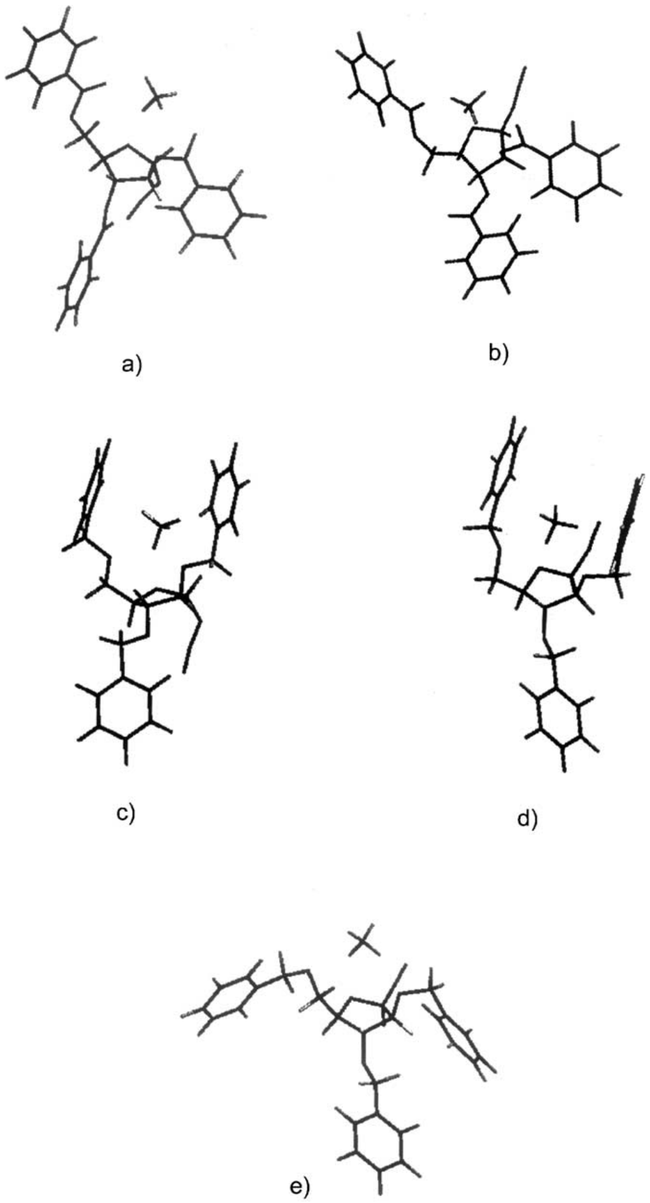


Fig. 4. Calculated structures of ammonium-bound monomers: (a) $[3\alpha NH_4]^+$, (b) $[3\beta NH_4]^+$, (c) $[4\alpha NH_4]^+$, (d) $[4\beta NH_4]^+$ and (e) $[4\beta NH_4]^{+\#}$ (activated monomer for about 10 kJ/mol becoming "similar" to $[3\beta NH_4]^+$).

expressed in the $\ln(k_A/k_B)$ values from −0.9 (5α) to +4.5 (4β) or in $R\Delta G^{c}_{rel}/T$ values from −4 to 37 $J\,mol^{-1}\,K^{-1}$.

The measured $\Delta G_{rel}/T$ values clearly show the difference between the 2- or 3-deoxy-ribo, xylo- and arabino-pentofuranosyl azide derivatives, i.e., the compounds 1, 5, 6 and 2, 3, and 4. The $\Delta G_{rel}/T$ values of the benzoyl (3) and of benzyl (4) derivatives of l-azido-arabino-furanose are also significant. 1β-Azido-anomers of all measured pairs have greater $\Delta G^{c}_{rel}/RT$ but with two exceptions of anomers 3 and 6.

The ammonium affinities (AAs) (Table 3) of compounds 1–4 obtained by the semi-empirical orbital method AM1 [25] qualitatively correlate with measured $\Delta G^{c}_{rel}/RT$ values (see Table 2, last column) of all compounds, but for anomers 4 where these values are completely opposed. The differences in AAs between appropriate compounds are small (e.g., lα and 1β anomers), though ΔAA of both anomer 3 are qualitatively correlated. The calculated ΔAAs of pairs of compounds 2 and 3 correspond to measured relative free energies of monomers, though it seems that the AAs of 3α and 2β are also too low. Our previous study [13] shows that AAs of anomer 4 are relatively correct.

The semi-empirical orbital method (AM1) is known as a low level calculation of thermochemical properties of molecules and ions, so AA values could be unreliable. However, Choe et al. [29] demonstrated that AM1 calculations of complexation propensities of calixarene derivatives toward alkylammonium ions gave the same trend as ab initio HF/6-31g calculations and with experimental data. AM1 method was used for performing the geometry optimization which was then used as initial coordinates for full electronic structure optimization the higher level [30].

We believe that AM1 calculations of monomers (Fig. 4a–c) give reasonable position of the ammonium ion and of hydrogen bonds in clusters. Fig. 4a and b show the structures of the most stable $3\alpha NH_4^+$ and $3\beta NH_4^+$ monomers calculated by the AM1 method where the ammonium ion is attached on the β side of both anomers. Vacant space above and on the left of the monomer is available for attaching the second or even the third or forth molecule of arabino-pentofuranosyl azide to the unbound hydrogen atoms of ammonium ion. On the contrary, ammonium ion in the $4\alpha NH_4^+$ and $4\beta NH_4^+$ monomers (Fig. 4c and d) is captured at least on two sides by the phenyl rings of *O*-benzyl substituents, which stabilize the monomer by cation-π electron (of benzene ring) interactions [31]. The low level AM1 method gives the same distance (0.3 μm) between nitrogen atom and both benzene rings of benzyl groups (Fig. 4c and d) as it is found in the synthetic NH_4^+ receptor [31]. Fig. 4 explains the formation of dimers, trimers and also tetramers of the anomers 3 (and also of the compounds 1, 2, 5 and 6), but it may also explain a complete absence of the peaks of trimers and tetramers in ESI mass spectra of compounds 4α and 4β. The calculated ammonium affinity values of the compounds 4α and 4β are the lowest of these series of compounds though the measured relative free energies $\Delta G^{c}_{rel}(4\alpha)$ and $\Delta G^{c}_{rel}(4\beta)$ are high and slow dubious values (see Table 2) which also depend on the reference compound present in dimer. The difference of $\Delta G^{c}(A,B)$ and $\Delta AA(A,B)$ can be interpreted by term $T\Delta(\Delta S_A)$ or by difference of transition states barriers of both dissociation channels.

The typically $\Delta(\Delta S_A)$ values Eq. (6) between the compounds 2 or 3 and anomers 1 are from 0 to $5\,J\,mol^{-1}\,K^{-1}$ (with the calculated ΔAA and estimated $T = 500\,K$) while for anomers 4 and 1 or 3 $\Delta(\Delta S_A(4, 1 \text{ or } 3))$ are in the range from 30 to $50\,J\,mol^{-1}\,K^{-1}$. Regardless to the presuming both values precision, this large entropy change of the formations of the ammonium-bound monomers of the 4α and 4β points to higher energy barrier of the transition state $[(4X)\cdots{}^{+}NH_4(1X)]^{\#}$, i.e., high difference between activation entropies $S^{\#}$ or activation free energies $\Delta G^{\#}$ of reaction channel for $[(lx)–NH_4]^+$ or $[(3x)–NH_4]^+$ product-ion formation from a $[(4x)–NH_4–(lx)]^+$ or $[(4x)–NH_4–(3x)]^+$ dimers ($x = \alpha$ or β). However, the information of the difference in the entropy of activation or of the activation free energy for reverse reaction ($\Delta G^{\#}$) obtained from the data of ammonium affinities (Table 3) and calculated structures of monomers has only qualitative sense. Since Fig. 4a and b shows the structures of $[(3x)NH_4]^+$ monomers with two unbound ammonium hydrogen atoms, a “similar” structure of $[(4x)NH_4]^+$ ion could be obtained only by increasing internal energy of this monomer for about $10\,kJ\,mol^{-1}$. Fig. 4c or d represents the most stable $[(4x)NH_4]^+$ monomers (Table 3) and Fig. 4e the activated $[(4\beta)NH_4]^{+\#}$ monomer which has a “similar” structure like $[(3\beta)NH_4]^+$ monomers. Thus, the reactive $[(4)NH_4(1)]^+$ or $[(4)NH_4(3)]^+$ dimers possess different transition states for competitive dissociation channels which are not interconvert and therefore different activation energies for reverse reactions.

3.2.3. Competitive CID-MIKE product-ions of $[A_2NH_4B]^+$ and $[A_3NH_4]^+$ trimers

The product-ions of ammonium-bound trimers $[A_2NH_4B]^+$ and $[A_3NH_4]^+$ (Fig. 5) were obtained by collision-induced fragmentation of parent ions. The fragmentations of the trimers are described by reactions 9(a)–9(d) and 10(a) and 10(b) and the relative free energies of ammonium clustering processes to dimeric and monomeric molecules are obtained by Eqs. (11a)–(11e) [21,22]:

- Hetero-trimer

$$[A_2NH_4B] \rightarrow (A)_2NH_4{}^{+}{+}B, \quad k_{A_2}\ (1) \tag{9a}$$

$$[A_2NH_4B] \rightarrow BNH_4{}^{+}{+}(A)_2, \quad k_{B}\ (1) \tag{9b}$$

$$[A_2NH_4B] \rightarrow ANH_4{}^{+} + (A+B), \quad k_{A}\ (2) \tag{9c}$$

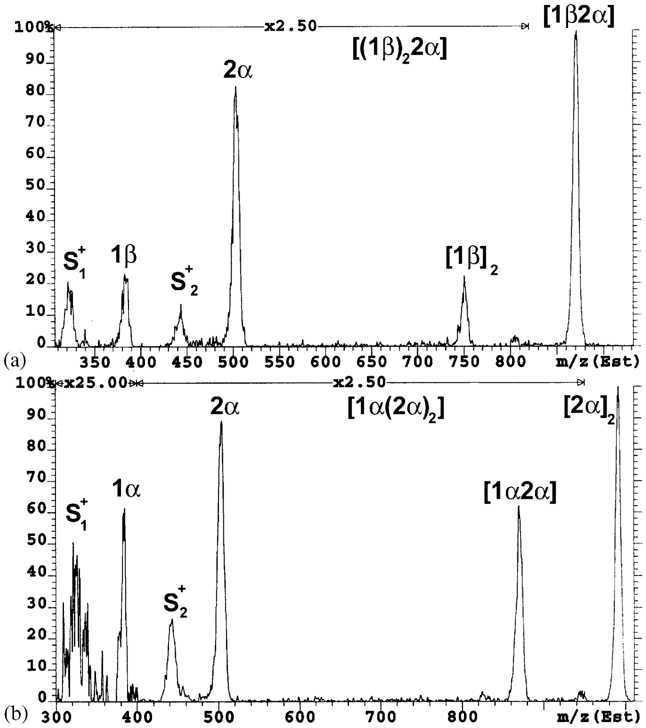


Fig. 5. CID-MIKE spectra of trimers: (a) $[(1\beta)_2NH_42\beta]^+$ and (b) $[l\alpha NH_4(2\beta)_2]^+$.

$$[A_2NH_4B] \rightarrow ANH_4B^{+} + A, \quad k_{AB}\ (2) \tag{9d}$$

- Homo-dimer

$$[A_3NH_4]^{+} \rightarrow A_2NH_4{}^{+}{+}A, \quad k_{A_2}\ (3) \tag{10a}$$

$$[A_3NH_4]^{+} \rightarrow ANH_4{}^{+} + A_2, \quad k_{A}\ (3) \tag{10b}$$

The numbers within parentheses indicate the number of reaction channels.

The relationship between products (reactions 9(a)–9(d)) is described in the following equations:

- Hetero-trimer

$$\ln\left(\frac{[A_2NH_4{}^{+}]}{[BNH_4{}^{+}]}\right) = \ln\left(\frac{k_{A_2}}{k_B}\right) = G^{c}(A_2) - G^{c}(B) = \Delta G^{c}(A_2, B) \tag{11a}$$

$$\ln\left(\frac{[ABNH_4{}^{+}]}{[ANH_4{}^{+}]}\right) = \ln\left(\frac{k_{AB}}{k_A}\right) = G^{c}(AB) - G^{c}(A) = \Delta G^{c}(AB, A) \tag{11b}$$

$$\ln\left(\frac{[ANH_4{}^{+}]}{2[BNH_4{}^{+}]}\right) = \ln\left(\frac{k_A}{2k_B}\right) = G^{c}(A) - G^{c}(B) = \Delta G^{c}(A, B) \tag{11c}$$

$$\ln\left(\frac{[A_2NH_4{}^{+}]}{2[ANH_4{}^{+}]}\right) = \ln\left(\frac{k_{A_2}}{2k_A}\right) = G^{c}(A_2) - G^{c}(A) = \Delta G^{c}(A_2, A) \tag{11d}$$

- Homo-dimer

$$\ln\left(\frac{[A_2NH_4{}^+]}{[ANH_4{}^+]}\right) = \ln\left(\frac{k_{A_2}}{k_A}\right) = G^c(A_2) - G^c(A) = \Delta G^c(A_2, A) \qquad (11e)$$

The new set of reactions and equations are obtained by alternating A with B in Eqs. (9a)–(9d). The rate constants of monomers formations k_A and k_B represent the intensities of the monomer peaks and the S^+ peaks as it is shown in Eq. (4). Although effective temperature (T) of CID-activated trimers is unknown, it is possible to calculate the ratio between T of dimers (T_D) and of trimers (T_T) from Eqs. (4) and (11b). Both equations combined give [21]: $RT_T = [G^c(A) - G^c(B)]/[\ln(k_{A_2}/k_B) - \ln(k_{A_2}/k_A)]$; ($k_{A_2}/k_B$ and k_{A_2}/k_A from Eqs. (11a) and (11e). From $[G^c(A) - G^c(B)] = RT_D\ln(k_A/k_B)$ (Eq. (4)), the final Eq. (12a) represents

$$\frac{T_T}{T_D} = \frac{\ln(k_A/k_B)}{\ln(k_{A_2}/k_B) - \ln(k_{A_3}/k_A)} \qquad (12a)$$

Change of A and B in Eq. (12a) gives another equation (12b, not shown). The third variant for T_T/T_D ratio is obtained from Eq. (11b) and by exchange of A and B in 11b as follows:

$$\frac{T_T}{T_D} = \frac{\ln(k_A/k_B)}{\ln(k_{AB}/k_B) - \ln(k_{AB}/k_A)} \qquad (13a)$$

k_{AB} and k_B from $[ANH_4B_2]^+$, k_{AB} and k_A from $[A_2NH_4B]^+$).

The calculated ratios of effective temperatures (T_T/T_D) are about 0.85 for the $[(1)NH_4(2)_2]^+$ types dimers and about 0.75 for $[(1)_2NH_4(2)]^+$ dimers. However, where T is defined as the average internal energy of reactive ions, these effective temperature ratios indicate a small difference in stability of different types of ammonium-bound trimers and also that the trimers are less stable than the dimeric ammonium-bound clusters.

Intensities of product-ion peaks in CID-MIKE spectra of the timers are shown in Table 4 and two examples are shown in Fig. 5. The logarithmic ratios (ln) of the corresponding competitive product-ion peak intensities (or rate constants) are shown in Table 5. The $\ln(k_A/2k_B)$ values (Eq. (11c)) of monomers shown in Table 1 (last two columns) are practically the same as the $\ln(k_A/k_B)$ values (Eq. (4)) of dimers (ibid., column 4). Small differences in ΔG^c(A,B) values obtained from dimeric or trimeric ammonium-bound clusters are probable attributed to serious experimental errors. Namely, the relative low peak intensities of monomers obtained by the dissociations of trimers (Table 4) can be a result of experimental errors. However, nearly the same ΔG^c_{rel}(M) values obtained by kinetic method regardless the measuring of dissociation products of dimers or trimers (reactions 3 or 11c, respectively) confirm this approach to be quite appropriate for studying cluster ions. Also the same ratios of rate constants of monomers formed from dimers or trimers evidently show that an individual molecule is bound in different clusters with relatively the same binding energy.

$\Delta G^c_{rel}/RT$ values of dimers shown in columns 4–6 in Table 5 are normalized to the $\Delta G^c_{rel}(1\alpha)/RT = 0$. Two different series of $\Delta G^c_{rel}/RT$ values of $[ANH_4B]^+$ hetero-dimers (Table 5, column 4) and of $[(A)_2NH_4]^+$ homo-dimers (ibid., columns 5 and 6) which depend on the reaction pathways of their formation, can be explained only by the difference in energy barriers of two reaction channels. In the decomposi-

Table 4
Abundances of competitive CID-MIKE product-ions of $[(A)_2NH_4B]^+$ trimers

Trimeric ion $[NH_4{}^+]$		Rel. int. (%) [neutral(s) × NH_4]$^+$			
$[(A)_2]$	[B]	Dimer		Monomer	
		[AB]	$[(A)_2]$	$[A](S_{A_1}{}^+)$[a]	$[B](S_B{}^+)$[a]
1α	1α		100	32 (9)	
1β	1β		100	40 (15)	
2α	2α		100	39 (16)	
2β	2β		100	44 (16)	
3α	3α		100	45 (12)	
3β	3β		100	34 (13)	
1α	2α	100	11	13 (5)	48 (6)
1α	2β	100	5	9 (4)	54 (2)
1β	2α	100	9	17 (8)	32 (4)
1β	2β	100	5	16 (7)	57 (9)
2α	1α	25	100	47 (11)	3.8 (2)
2α	1β	30	100	52 (13)	9 (4)
2β	1α	10	100	44 (14)	2 (1)
2β	1β	17	100	47 (14)	4.5 (3)
1β	3α	100	4.5	9 (5)	51 (6)
3α	1β	9	100	40 (10)	<1
3β	1α	11	100	37 (8)	<1
3β	1β	10	100	33 (8)	<1

[a] A portion of furanosyl fragment ion peak ($S_i{}^+$) participates to intensity of monomer.

Table 5
Logarithms (ln) of rate constants ratio (or ln of competitive production peak intensitie ratios) of ammonium-bound trimers: $[(A)_3NH_4]^+$ and $[(A)_2NH_4B]^+$

Parent ions trimers		Product ions ln [of rate constants ratio]			
		$k_A/2k_B$	$[k_{AB}/k_A]^*$	$[k_{A_2}/k_B]^*$	$[k_{A_2}/k_A]^*$
Homo					
$[(A)_2]$	[B]				
1α	1α				1.1
1β	1β				1.6
2α	2α				2.9
2β	2β				3.2
3α	3α				4.0
3β	3β				4.0
		Monomers	Dimers		$[k_{A_2}/2k_A]$
Hetro			Hetro	Homo	
1α	2α	−2.0	2.0	0.5	0.5
1α	2β	−2.5	2.5	0.0	0.1
1β	2α	−1.3	2.5	0.7	0.7
1β	2β	−1.8	2.5	0.0	0.2
1β	3α	−2.4	3.1	0.8	0.7
2α	1α	1.8	1.4	3.0	3.4
2α	1β	1.1	1.4	3.1	3.4
2β	1α	2.5	0.9	3.6	3.9
2β	1β	1.7	1.4	3.7	3.9
3α	1β		1.7		4.9
3β	1α		2.0		4.8
3β	1β		1.8		4.9

The logarithms of intensity ratios are normalized to $\ln[1\alpha NH_4{}^+] = \ln k_{1\alpha} = 0$.
Normalization is preformed by addition of the $\ln([k_i]/[k_{1\alpha}])$ to the obtained $\ln[k/k_i]$ value (e.g., $\ln[k_A/2k_B] + \ln[k_B/k_{1\alpha}]$).

tion of the $[(1\alpha)_2NH_4(2\alpha)]^+$ and $[(1\alpha)NH_4(2\alpha)_2]^+$ trimers to the same $[(1\alpha)NH_4(2\alpha)]^+$ hetero-dimer the measured $\Delta G^c_{rel}/RT$ are 2.0 and 1.4 (Table 5), respectively. The difference of 0.6 in $\Delta(\Delta G^c_{rel})/RT$ in this example and 1.1–1.6 obtained for the other dimers (Table 5, column 4) are probably caused by the difference in free energy of activation ($\Delta G^{\#}$) of these fragmentations. Namely, the loss of the 1α or 1β molecule, which forms less stable ammonium-bound monomer (lower ΔG^c_{rel}) is the most prevailing process of hetero-dimer formation from trimeric ion. Thus, a hetero-trimer, e.g., the $[(1\alpha)_2NH_4(2\alpha)]^+$ composed of the two molecules of lower ΔG^c_{rel} (e.g., 1α) and of a molecule of higher ΔG^c_{rel} (e.g., 2α) mostly decomposes to hetero-dimer ($[l\alpha NH_4(2\alpha)]^+$), but the loss of the neutral molecules, such as 2α or 2β is less favored. The formation of homo-dimeric ions has the same effect.

In this case, the obtained $(\Delta G^c)/RT$ values of $[(2\alpha)_2]$ are higher in the dissociation of $[(1\alpha)NH_4(2\alpha)_2]^+$ hetero-trimer than of $[(2\alpha)_3NH_4]^+$ homo-trimer. The highest values of ΔG^c of $[(1\alpha)_2]$ and $[(1\beta)_2]$ homo-dimers are obtained from the dissociations of $[(1\alpha)_3NH_4]^+$ and $[(1\beta)_3NH_4]^+$ homo-trimers. The hetero-trimers which compose one molecule of lower ΔG^c value, e.g., 1α in $[(1\alpha)NH_4(2\alpha)_2]^+$ give the higher ΔG^c values for the $[(2\alpha)_2NH_4]^+$ or $[(2\beta)_2NH_4]^+$ homo-dimer than those of $[(2\alpha)_3NH_4]^+$ or $[(2\beta)_3NH_4]^+$ homo-trimers (Table 5). Thus, the differences in the free energy of activation or energy barriers of transition states of trimers determine the obtained ΔG^c values of dimers. The order of ammonium-bound dimers stabilities with the highest ΔG^c values obtained from more reactive trimers are: $(1\alpha)_2 < (1\beta)_2 < (1\alpha 2\alpha) < (1\alpha 2\beta) = (1\beta 2\alpha) = (1\beta 2\beta) < (2\alpha)_2 < (2\beta)_2 < (3\beta)_2 = (3\alpha)_2$.

4. Anomeric and substituents effects on stabilities of monomers and dimers

4.1. Anomeric effects

The anomeric effect is important for the analyses of these compounds. An anomeric pair which is also diastereomeric pair could not be measured directly with the comparison of product ion abundances of a homo-dimer, because the same molecular masses of product monomers prevent their mass spectrometric recognition. The recognition of anomers from hetero-dimers or from hetero-trimers based on relative stability of particular anomers is throughout possible. The branching ratio ($R_{A,B}$) [19] leading to formation of the two fragments from two dimers is given in equation: $R_{A,B} = [A/C]/[B/C]$. Anomers A and B are in pairs with reference compound C which forms the ammonium-bound dimers [AC] and [BC]. The $R_{A,B} = [k_A/k_C]/[k_B/k_C] = [k_A/k_B] = \exp[\Delta G^c(A, B)]/RT = \exp[\Delta G^c_{rel}(A) - \Delta G^c_{rel}(B)]/RT$. For the trimer $[A_2NH_4B]^+$ this $R_{A,B}$ is straightforward equal to $[k_A/2k_B]$ (Eq. (11c)), where $(k_A/2)$ is used because monomer A is obtained from trimer by two reaction channels. The $R_{A,B}$ values for these compounds are from 1.2 (3α and 3β) to 2.0 (1β and 1α).

4.2. The substituent effects on order of stability of monomers

Apparent effects of number of protecting groups and their *p*-substituents on ΔG^{c} values are seen from the data in Table 2. Four benzoyl groups present in xylo- and arabinofuranosyl-azides (anomers 2 and 3) increase the stability of these monomers in comparison to monomers 1, 5 and 6. The *p*-substituents of protecting groups' considerably affect the stability of monomers and show the importance of electron density of carbonyl oxygen on the number and strength of hydrogen bonds in monomers. The order of monomer stabilities: $5\alpha < 5\beta < 1\alpha < 1\beta < 6\beta < 6\alpha$, which is the same as the proton affinities of the corresponding *p*-substituted benzoic acids or their methyl esters [4], unambiguously shows the electron withdrawing or donating properties of *p*-(Cl, or H of CH_3) substituents.

5. Conclusion

Electrospray ionization has been demonstrated to be a very efficient method for the transfer of weakly bound non-covalent complexes from solution to the gas-phase. In the presence of ammonium acetate in methanol solution of anomeric 1α- or 1β-azido-pentofuranosyl derivates the peaks characteristic of monomeric, dimeric and trimeric ammonium-bound complex ions are present in high intensities in the ESI mass spectra. Applying kinetic method to the competitive product-ions abundances obtained from ammonium-bound dimers or trimers gives relative free enthalpies (ΔG^{c}) of ammonium attached to one or two molecules of pentofuranosyl-azides, respectively. Comparison of the ΔG^{c} with calculated ammonium affinities of these compounds shows that both thermodynamic quantities do not correlate in some cases. The main reasons for these disagreements are the differences in activation barriers of competitive dissociations of ammonium-bound complex-ions.

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