Supporting Information for

Towards closing the Gap between Hexoses and *N*-Acetylhexosamines: Experimental and Computational Studies on the Collision-Induced Dissociation of Hexosamines

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S1. Fragments in the Low Mass Range

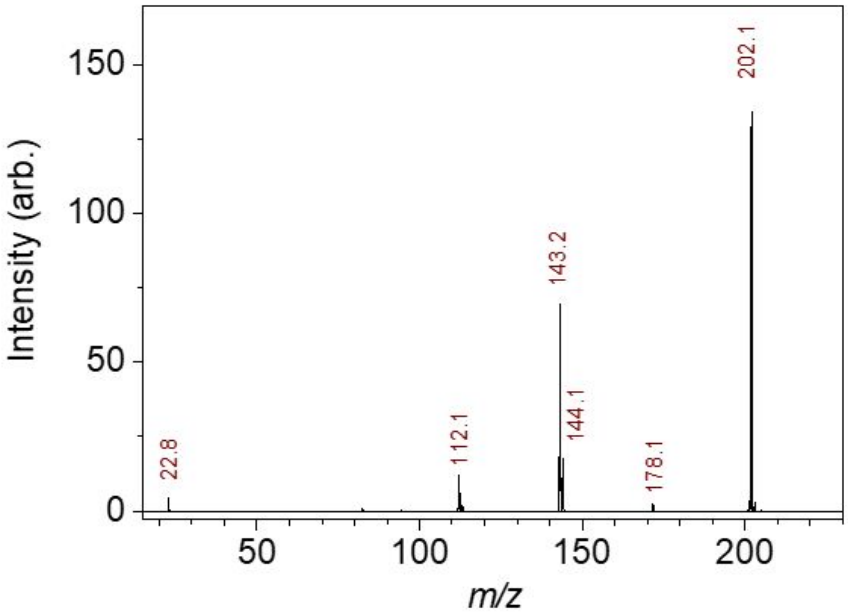

Figure S1. A tandem quadrupole mass spectrometer (Bruker Daltonics Esquire 3000 plus ion trap mass spectrometer, Billerica, MA, USA) was used for low mass fragment measurement of glucosamine. The mass spectrum shows that sodium ion (m/z 22.8) is the only major ion observed in the range from m/z 15 to 100.

S2. Structural Details Obtained from Calculations at MP2 Level

S2.1. Glucosamine in Ring-Form

The geometries of the most important minima and TS structures for GlcN in ring-form are shown in Figure 5 of the main text. In the following, a rough discussion of the geometries is provided. The most stable geometries of sodiated α- (**a-GlcN_m**) and β-GlcN (**b-GlcN_m**) feature the same structural motive: The Na^+ ion is coordinated to O3 and O4. In addition, the former O atom acts as an H donor for a hydrogen bond to O6, while the latter has its H pointing (roughly) in the direction of the amino group. Upon desodiation, the most stable geometry only changes slightly, the most striking difference is the orientation of the OH group at O4: Instead of forming a hydrogen bond to O6, it now points towards O3. The deamination of both anomers proceeds via the H transfer from O1 to the amino group. In the initial states **a-GlcN_nd3_i** and **b-GlcN_nd3_i**, the Na^+ is coordinated to O1 and O6, the H atom at O1 roughly points in the direction of the amino group, with an N-H distance of 2.01 Å and 2.31 Å, respectively. These values decrease to 1.02 Å in the corresponding TS structures **a-GlcN_nd3_t** and **b-GlcN_nd3_t** indicating that the N-H bond has already been formed. At the same time, the C2-N bond being broken is elongated to 2.07 Å in **a-GlcN_nd3_t** and 2.00 Å in **b-GlcN_nd3_t**, respectively. A further interesting detail is the fact that during the reaction, the C1-O5 bond breaks to form a five-membered ring with a bond between C2 and O5. In the TS structures, the interatomic distances between C2 and O5 are calculated to be 1.93 Å for the α- and 1.91 Å for the β-anomer. The ring-opening reaction is a further reaction, for which both α- and β-GlcN proceed via a similar mechanism. However, due to the difference in the stereochemistry, the initial states for the ring-opening reactions differ slightly. In both **a-GlcN_ro_i** and **b-GlcN_ro_i**, the proton at O1 is pointing towards O5, with a distance of 2.42 Å and 2.37 Å, respectively. In the former case, the Na^+ is

coordinated between O1 and the amino group, whereas in the latter structure, Na^+ is coordinated between O1 and O3. In the TS structures, **a-GlcN_ro_t** and **b-GlcN_ro_t**, the H at O1 is already closer to O5 than to O1. At the same time the C1-O5 bond is already being elongated from 1.39 Å in the initial state geometries for both α- and β-anomer to 1.55 Å and 1.54 Å, respectively. Different to the reaction channels discussed above, the dehydration of α- and β-GlcN proceed via different reaction channels. Whereas the former reacts via the O4 to O1 H transfer, the latter involves the H transfer from O3 to O1. The structure **a-GlcN_d2o_i** is characterized by the coordination of O4 to the Na^+ and the circumstance that the H atom of O4 points into the direction of O1, with an O1-H distance of 1.73 Å. At the TS **a-GlcN_d2o_t**, the H atom is closer to O1 than to O4, as the bond length O1-H of 1.03 Å indicates. At the same time, the C1-O1 bond is essentially broken, with a bond distance of 2.46 Å. In **b-GlcN_d2o_i**, the Na^+ is coordinated to O3 and O6. Although the H at O3 is the H atom being transferred to O1, the O1-H distance is still relatively long here, 3.05 Å. In the TS **b-GlcN_d2o_t,** the H is essentially located at O1 with an interatomic distance of 1.02 Å. At the same time, the so formed water molecule has more or less left the original sugar molecule, as the C1-O1 distance of 2.87 Å shows. The water molecule is only weakly interacting with O3 via a hydrogen bond of 1.52 Å.

S2.2. Glucosamine in Linear Form

The geometries derived from liner GlcN are shown in Figure 6 of the main text. The most stable conformer of sodiated linear GlcN, **l-GlcN_m**, features the Na^+ ion coordinated by O4, O5, and O6. In addition, the structure is stabilized by two H bonds, in one O4 donates an H to the amino group, in the other O6 donates an H to O3.

For the most favorable ND_3 deamination reaction proceeding via the H transfer from O3 to the amino group, the IS **l-GlcN_nd3_i** features the Na^+ at O1 and O3.

Furthermore, the H atom at O3 forms an H bond with the N atom, which is 2.03 Å long. At the TS, **l-GlcN_nd3_t**, the H atom is transferred to the N as indicated by an N-H distance of 1.03 Å. The breaking C2-N bond is elongated from the equilibrium distance of 1.47 Å to 2.05 Å in the TS. A further interesting aspect is that the deamination step comes along with the rearrangement of the H atom at C3 to C2. At the TS, the H atom is located between C2 and C3 with distances of 1.52 Å and 1.26 Å to C2 and C3, respectively. The most preferred ND_2H deamination channel starts from a geometry, **l-GlcN_nd2h_i**, in which O1, O3, O4, and O6 coordinate to the Na^+. As the H atom being transferred in this reaction is located at C3, the Na^+ position likely only has a weak influence on the height of the reaction barrier. In the IS, the H at C3 is roughly aligned with the amino group. In the corresponding TS **l-GlcN_nd2h_t**, one sees the H atom at the N atom, while the C2-N bond is about to break, as shown by the bond length of 1.64 Å. For the dehydration via the D_2O pathway, the IS of the most likely mechanism **l-GlcN_d2o_i** has the Na^+ coordinated to the amino group, O1, and most importantly, O5, which also acts as H donor in an H bond with O6. At the TS **l-GlcN_d2o_t**, the H atom of O5 has been transferred to O6 to form water, which features a C6-O6 bond distance of 1.83 Å. In the DHO dehydration channel involving the H transfer from C2 to O3, the most favorable reaction requires a starting geometry (**l-GlcN_dho_i**), in which the crucial feature is the interaction between Na^+ and O1. Apart from that, the Na^+ also interacts with the amino group and O6. However, only the coordination to the carbonyl O atom O1 leads to the enhancement of the C-H acidity at C2. The corresponding H atom is 2.46 Å away from O3, which is in vicinal position. In the TS **l-GlcN_dho_t**, the H is moving from C2 to O3 as indicated by the C2-H and the O3-H distances of 1.58 Å and 1.17 Å, respectively. At the same time, the C3-O3 bond is, with a bond distance of 1.54 Å, slightly elongated compared to the equilibrium distance of 1.41 Å. The

most favorable ^{0,2}A cross-ring cleavage reaction starts from the structure **l-GlcN_02_i**, in which the Na^+ is interacting with O4, O5, and in particular O3, which transfers an H atom to O1 during the reaction. In the IS, the H atom at O3 is 2.25 Å away from O1; the distance decreases to 1.05 Å in the TS while the O3-H distance increases from 0.97 Å to 1.41 Å. Simultaneously to the H transfer, the C2-C3 bond is being elongated from 1.54 Å to 2.07 Å in the TS **l-GlcN_02_t**, ultimately leading to the scission of the C-C bond. The first step of the ^{0,3}A cross-ring dissociation features an IS geometry, **l-GlcN_03e1_i**, in which the Na^+ is coordinated by O3, O4, O5, and O6, or in other words: the Na^+ is not in the direct vicinity of the reacting moiety at C1 and C2. In this geometry, the H at C2 is 1.58 Å away from C1, while the C2-H bond is 1.10 Å. At the TS **l-GlcN_03e1_t**, the H is located between C1 and C2 with interatomic distances of 1.25 Å to C1 and 1.53 Å to C2. A further interesting detail is the H-N-H angle at the amino group. In the IS, the angle is 110°, while the angle increases to 117° in the TS. This can also be interpreted as a sign for the rehybridization of an sp^3 N to an sp^2 center. This would correspond to the formation of a zwitterionic structure with an iminium group at C2 as discussed for galactosamine (see Figure 9 of the main text). However, the IRC analysis yields a product structure with an epoxy group at C1 and C2 for this reaction. Here the H-N-H angle is 110° again, indicating the presence of an sp^3 N center. This structure, **l-GlcN_03e2_i**, is also the initial state for the second step in the ^{0,3}A cross-ring cleavage, featuring the H at O4 2.57 Å away from the epoxy O. In the TS, that H has moved to the epoxy O atom, with a distance of 0.99 Å, which also results in the opening of the epoxy ring; in the TS, **l-GlcN_03e2_i**, the O atom is only bound to O1. At the same time, the C3-C4 bond is about to be broken with an interatomic distance of 1.91 Å.

S2.3. Galactosamine in Ring-Form

The geometries of the most important minima and TS structures for GalN in ring-form are shown in Figure 8 of the main text. Different to GlcN, the most stable geometries for sodiated α- and β-GalN (**a-GalN_m** and **b-GalN_m**) coordinate the Na^+ ion via O4, O5, and O6, without any well-defined hydrogen bond. The most favorable structures without the ion are very similar to their sodiated counterparts, with some small differences in the orientation of the OH/NH_2 groups. The deamination channel of GalN proceeds similarly to GlcN, namely via the H transfer from O1 to the amino group accompanied by a rearrangement of the six-membered ring to a five-membered ring with a bond between O5 and C2 instead of between O5 and C1. Also here, the IS structures, **a-GalN_nd3_i** and **b-GalN_nd3_i**, have the Na^+ ion coordinated to O1 and O6. The distance between the H at O1 and the N atom are 2.73 Å and 2.22 Å, respectively. At the corresponding TS structures, **a-GalN_nd3_t** and **b-GalN_nd3_t**, the NH bonds of the leaving ammonia molecule are already formed, as indicated by bond lengths of 1.02 Å in both structures. Furthermore, one sees from the TS geometries how O5 substitutes the C2-N bond. For the α-anomer, the C2-O5 bond length and the C2-N bond length are 2.06 Å and 1.91 Å, respectively. The values found for the β-anomer are comparable, 1.99 Å and 1.90 Å. For the ISs of the ring-opening reactions of GalN, we see the same differences in the Na^+ coordination as observed for GlcN: the Na^+ is coordinated by O1 and the amino group in the α-anomer, whereas the β-anomer coordinates Na^+ via O1, O3, and O4. The distance between O5 and the H at O1 are 2.42 Å in **a-GalN_ro_i** and 2.51 Å in **b-GalN_ro_i**. Similar to GlcN, we also see here that the H is already closer to O5 than to O1 in the associated TSs **a-GalN_ro_t** and **b-GalN_ro_t**. The breaking bond between C1 and O5 features a length of 1.57 Å and 1.58 Å at the TS, respectively. Despite the difference in the stereochemistry at C4, the most favorable dehydration

channel of α-GalN proceeds via the same dehydration channel as α-GlcN, namely the H transfer from O4 to O3. Similar to **a-GlcN_d2h_i**, **a-GalN_d2h_i** features the Na^+ between O4 and O6. However, the distance between the H at O4 is, with a distance of 1.76 Å, closer to O3 than the corresponding value for **a-GlcN_d2h_i**, which is a direct consequence of the different stereochemistry at C4. In the TS **a-GalN_d2h_t**, the H atom is already at O3 to form the leaving water molecule. The C3-O3 bond is also elongated, from 1.44 Å in the IS, to 2.05 Å at the TS structure. Different from β-GlcN, the most likely dehydration channel of β-GalN involves the proton transfer from O4 to O1 (instead of O3 to O1). In the IS state **b-GalN_d2h_i**, the Na^+ is coordinated to O4 and O6, with the former acting as an H donor in a hydrogen bond to O1, featuring an O1-H distance of 1.77 Å. At the TS **b-GalN_d2h_t**, the leaving water molecule is already formed and only interacts via a hydrogen bond to O4, which is 1.41 Å long. In contrast, the original C1-O1 bond is more or less already broken as indicated by the atomic distance of 2.30 Å.

S2.4. Galactosamine in Linear Form

As visible from the geometries in Figure 9 of the main text, the most stable structure of sodiated, linear GalN **l-GalN_m** features the Na^+ coordinated to O1, O4, O5, and O6. A hydrogen bond from the H at O5 to the amino group further stabilizes the structure. Although the ND_3 deamination channel of both GlcN and GalN involves the H transfer from O3 to the neighboring amino group, the Na^+ coordination is different in the two cases, while **l-GlcN_nd3_i** has the Na^+ bound to O1 and O3, it is O3, O4, and O5 which interact with Na^+ in **l-GalN_nd3_i**. The coordination to O3 facilitates the H transfer to the amino group, which is 1.82 Å away from the H atom at O3. All in all, the molecular geometries of the IS and TS for the ND_3 deamination of GlcN and GalN, are relatively similar, despite the differences in the Na^+ coordination.

In the TS **l-GalN_nd3_t**, we also see that the H is already transferred to the leaving NH_3 molecule and that the H atom at C3 is moving to C2, as observed in **l-GlcN_nd3_t**. An even stronger similarity between GlcN and GalN can be observed for the ND_2H deamination pathway. Not only are the crucial atomic distances in TS and IS as marked in Figures 6 and 9 of the main text comparable with differences of less than 0.15 Å. Also the Na^+ ion coordinates to the same O groups at O1, O3, and O4. Owing to the differences in the H transfer, the D_2O dehydration of GalN involves different geometries than the corresponding reaction of GlcN. To facilitate the H transfer from O4 to O5, the Na^+ ion is coordinated to O1, O3, and O4 in the IS **l-GalN_d2o_i**. The H at O4 forms an H bond to O5, which is 1.98 Å long. Although the H is already transferred to O5 in the TS **l-GalN_d2o_t** as indicated by the O5-H distance of 1.05 Å, the leaving water molecule is still interacting with the sugar: The breaking C5-O5 bond is only elongated to 1.97 Å, and there is a hydrogen bond of 1.48 Å between the water molecule and O4. The DHO dehydration channel of GalN follows the previously discussed H transfer from C2 to O3. In the IS **l-GalN_dho_i**, the Na^+ ion coordinates to O1 and O5, despite the small difference to the Na^+ coordination in **l-GlcN_dho_i**, the atomic distances around the C2-O3 moiety are very similar in both structures. The associated TS structures feature more differences, the most striking one is the fact that the water molecule being eliminated in **l-GalN_dho_t** displays much larger interatomic distances to the remaining sugar molecule, C2-H: 2.37 Å and C3-O3: 1.86 Å, than the corresponding values in **l-GlcN_dho_t**, C2-H: 1.58 Å and C3-O3: 1.54 Å. Similar to the ND_2H deamination, the $^{0,2}A$ cross-ring dissociation of GlcN and GalN also feature very similar IS and TS geometries. Apart from the bond length of the H bond formed by the H at O3 and O2, which is with a value of 1.82 Å noticeably shorter in **l-GlcN_02_i**, the important interatomic distances in **l-GalN_02_i** and **l-GalN_02_t** differ by less than 0.4 Å form

those of **l-GlcN_02_i** and **l-GlcN_02_t**. The ^{0,3}A cross-ring dissociation of galactosamine starts with the IS **l-GalN_03z1_i**, which features the Na^+ coordinated to O4 and O5. The structure is further stabilized by H bonds between O4 and O1 and between O2 and the amino group. In this structure, the distance between the H atom at C2 and C1 is 2.12 Å, i.e., slightly longer than in **l-GlcN_03e1_i**. In the TS **l-GalN_03z1_t**, one re-encounters many structural motives known from **l-GlcN_03e1_t**, e.g., the H atom being between C1 and C2, as well as the enlarged H-N-H angle, which is 119° in the present case. An interesting difference is the position of the Na^+ at the TS, which is, with a Na-O1 distance of 2.17 Å, relatively close to O1. We assume that this interaction prevents the formation of an epoxy group as the intermediate of that reaction. In fact, we have not been able to obtain a product geometry form the IRC analysis. Thus we assume the formation of a zwitterionic intermediate with an alcoholate group at C1 and an iminium C2 group as the intermediate product of the ^{0,3}A cross-ring dissociation, similar to the TS structure **l-GalN_03e1_t**. The second step of the ^{0,3}A cross-ring dissociation start with a zwitterionic structure (**l-GalN_03e2_i**) that is comparable to **l-GalN_03e1_t**. In this geometry, the Na^+ is only 2.12 Å away from O1. In addition, the structure features an H bond from the H at O4 to O1 with a distance of 1.55 Å. At the TS **l-GalN_03e2_t**, the H has moved to O1, with a distance of 0.99 Å. At the same time, the C3-C4 bond is elongated from 1.56 Å in the IS to 2.00 Å in the TS.

S3. Reaction Barrier for Deuterium-Exachanged Isotopologues

As we are reporting reaction barriers corrected by the ZPE, there can be some differences in the barriers for different isotopologues. These differences may eventually become important for isotope-marking experiments, e.g., CID experiments with D_6-HexNs, i.e., HexNs with all H atoms at OH and NH_2 groups replaced by D, to determine the origin of the H atoms in the detected and eliminated fragments. To estimate this difference in the barriers, we have taken the IS and TS geometries optimized at MP2 level and replaced the H atoms in question by D and re-calculated the normal mode analysis. The results for D_6-HexN in ring-form are collected in Table S1, while the results for the linear sugars are in Table S2. As visible from the tables, the barriers tend to go up slightly upon replacing the H atoms by D. The largest change is found for the ring-opening of both α- and β-GlcN, for which the barriers go up by 4 kJ/mol, which is comparable to the accuracy of the quantum chemical calculations. In other words, the differences in the activation barriers of isotopologues are sufficiently small and can be neglected.

Table S1. Lowest barriers in kJ/mol of the studied dissociation channels for deuterium-substituted GlcN and GalN in ring-form calculated at MP2 level. Δ denotes the differences to the corresponding values calculated for the non-deuterium substituted species shown in Table 1 of the main text.[a] The differences in the barriers are coming from the mass-dependent zero point energies. In addition, the desodiation energies are also shown.

	D_6-GlcN				D_6-GalN			
	α	Δ	β	Δ	α	Δ	β	Δ
ND_3 deamination	218	-1	195	-1	216	-1	212	-1
D_2O dehydration	239	-1	220	0	246	-2	213	-2
Ring-opening	194	-4	183	-4	188	-2	177	-3
Desodiation energy	198	0	190	0	188	0	205	0

[a] Calculated as E(HexN)-E(D_6-HexN)

Table S2. Lowest barriers in kJ/mol of the studied dissociation channels of deuterium-substituted, linear GlcN and GalN calculated at MP2 level. Δ denotes the differences to the corresponding values calculated for the non-deuterium substituted species shown in Table 2 of the main text.[a] The differences in the barriers are coming from the mass-dependent zero point energies.

	D_6-GlcN	Δ	D_6-GalN	Δ
ND_3 deamination	272	-1	273	-1
ND_2H deamination	265	-1	261	0
D_2O dehydration	236	-1	253	-2
DHO dehydration	241	-1	247	0
C-C scission in ^{0,2}A cross-ring	157	-3	186	-2
C-C scission in ^{0,3}A cross-ring epoxy / *1,2*-zwitterionic	176 ,164	-1, -1	193, 174	-1, 0

[a] Calculated as *E*(HexN)-*E*(D_6-HexN)

S4. Details on the Calculation of RRKM Rate Constants

The calculation of the RRKM rate constants k as a function of the excitation energy E_{ex} follows Ref S1 and can be calculated with the following expression

$$k(E_{ex}) = G^{\ddagger}(E_{ex} - E_{TS} - E_r^{\ddagger})/hN(E_{ex} - E_r) \quad \text{(S1)}$$

Here, E_{TS} is the energy of the ZPE-corrected energy of the TS, referred to the IS of the reaction. $E_r^{\ddagger}$ and E_r are the rotational energies of the TS and IS, respectively. h stands for the Planck Constant. $N(E)$ is the density of states of the reactant, while the $G^{\ddagger}(E)$ is the sum of state of the TS with the contribution of the reaction coordinate omitted. One often applied approximation is to omit the rotational energies, so Equation S1 becomes:

$$k(E_{ex}) \approx G^{\ddagger}(E_{ex} - E_{TS})/hN(E_{ex}) \quad \text{(S2)}$$

If we treat the IS and the TS as s classical, uncoupled, harmonic oscillators, one can write for $G^{\ddagger}(E)$

$$G^{\ddagger}(E) = {E^{s-1}}\Big/\Big[(s-1)!\prod_{i=1}^{s-1} h\nu_i^{\ddagger}\Big] \quad \text{(S3)}$$

with $\nu^{\ddagger}_i$ being the real harmonic vibrational frequencies for the TS. Similarly, $N(E)$ becomes

$$N(E) = {E^{s-1}}\Big/\Big[(s-1)!\prod_{i=1}^{s} h\nu_i\Big] \quad \text{(S4)}$$

with ν_i being the harmonic vibrational frequencies for the IS. With these expressions, one can write for Equation S2:

$$k(E_{ex}) \approx \frac{(E_{ex} - E_{TS})^{s-1}}{(s-1)!\prod_{i=1}^{s-1} h\nu_i^{\ddagger}} \frac{(s-1)!\prod_{i=1}^{s-1} h\nu_i}{{E_{ex}}^{s-1}} \frac{1}{h}$$

$$= \frac{(E_{ex} - E_{TS})^{s-1}}{\prod_{i=1}^{s-1} \nu_i^{\ddagger}} \frac{\prod_{i=1}^{s-1} \nu_i}{{E_{ex}}^{s-1}} = \frac{\prod_{i=1}^{s-1} \nu_i}{\prod_{i=1}^{s-1} \nu_i^{\ddagger}} \left(\frac{E_{ex} - E_{TS}}{E_{ex}}\right)^{s-1} \quad \text{(S5)}$$

which is the final equation used to calculate the RRKM rate constants reported in the main text. In our study, we use, consistent with the definition of our reaction barriers,

the global minima of the α- and β-anomers as ISs for the reactions starting from the ring-form of a HexN. For reactions of linear HexNs we use the global minima of the linear form as IS.

S5. Barriers Re-evaluated at CCSD(T)//MP2 Level

Table S3. Lowest barriers in kJ/mol of the studied dissociation channels as well as the desodiation energies for GlcN and GalN in ring-form calculated at CCSD(T)//MP2 level.[a] Δ_{MP2} and Δ_{B3LYP} denote the differences to the corresponding values calculated self-consistently at MP2 and B3LYP level as shown in the main text.[b]

	GlcN						GalN					
	α	Δ_{MP2}	Δ_{B3LYP}	β	Δ_{MP2}	Δ_{B3LYP}	α	Δ_{MP2}	Δ_{B3LYP}	β	Δ_{MP2}	Δ_{B3LYP}
ND_3 deamination	198	18	-13	178	16	-16	199	17	-12	192	19	-14
D_2O dehydration	220	18	-29	205	15	-13	231	14	-20	198	14	-26
Ring-opening	187	4	1	176	3	5	181	4	-1	169	5	0
Desodiation energy	189	9	21	181	8	21	181	7	20	196	9	21

[a] Energies obtained via a single point calculation at CCSD(T) level at the geometry optimized at MP2 level. The zero-point energy correction used the values self-consistently obtained at MP2 level.

[b] Calculated as $\Delta_{MP2} = E_{MP2} - E_{CCSD(T)//MP2}$ and $\Delta_{B3LYP} = E_{B3LYP} - E_{CCSD(T)//MP2}$, respectively.

Table S4. Lowest barriers in kJ/mol of the studied dissociation channels of linear GlcN and GalN calculated at CCSD(T)//MP2 level.[a] Δ_{MP2} denotes the differences to the corresponding values calculated self-consistently at MP2 level as shown in the main text.[b]

	GlcN	Δ_{MP2}	GalN	Δ_{MP2}
ND_3 deamination	254	16	261	11
ND_2H deamination	261	2	258	3
D_2O dehydration	216	19	230	21
DHO dehydration	242	-3	235	12
C-C scission in ^{0,2}A cross-ring	156	-2	183	1
C-C scission in ^{0,3}A cross-ring epoxy */ 1,2-*zwitterionic	165, 156	10, 7	182, 165	10, 8

[a] Energies obtained via a single point calculation at CCSD(T) level at the geometry optimized at MP2 level. The zero-point energy correction used the values self-consistently obtained at MP2 level.

[b] Calculated as $\Delta_{MP2} = E_{MP2} - E_{CCSD(T)//MP2}$.

References

(S1) Henriksen, N. E.; Hansen, F. Y. *Theories of Molecular Reaction Dynamics: The Microscopic Foundation of Chemical Kinetics*; Oxford University Press, 2018.