

GAS-PHASE BASICITY MEASUREMENTS OF SINGLY- AND DOUBLY-CHARGED B_n FRAGMENT IONS USING ESI/FT-ICR MS

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INTRODUCTION

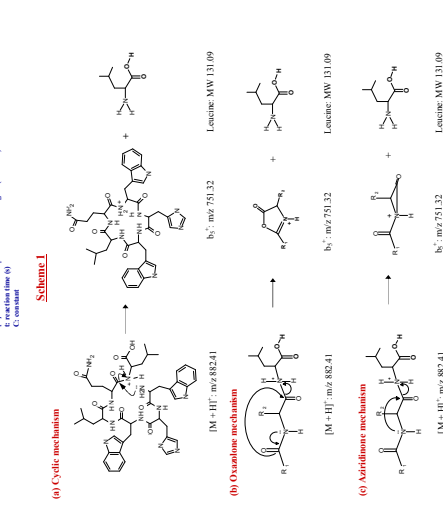
Recently, we reported on the possibility of accurately determining B_n fragment ions (cyclic and acyclic) using a combination of ion mobility spectrometry (IMS) and ion trap mass spectrometry (ITMS). In this paper, we report on the gas-phase basicity (GB) of B_n fragment ions and the relative intensity of protonated pyrolic ions in the presence of DPEEA. The gas-phase basicity (GB) of B_n fragment ions was determined using the relative intensity of protonated pyrolic ions in the presence of DPEEA.

EXPERIMENTAL

Instrumentation: ESI/FT-ICR mass spectra were acquired with an open-ended cylindrical Paul trap (Oronon FT-ICR, Orono, ME). The mass spectrometer was equipped with an open-ended cylindrical Paul trap (Oronon FT-ICR, Orono, ME). The mass spectrometer was equipped with an open-ended cylindrical Paul trap (Oronon FT-ICR, Orono, ME). The mass spectrometer was equipped with an open-ended cylindrical Paul trap (Oronon FT-ICR, Orono, ME).

Substrate: Benzamide, 18. All of the chemical substrates and reagents were purchased from commercial sources and used without any further purification, except for trifluoroacetic acid (TFA) which was distilled under reduced pressure. The relative intensity of protonated pyrolic ions in the presence of DPEEA was determined using the relative intensity of protonated pyrolic ions in the presence of DPEEA.

Scheme 1



RESULTS and DISCUSSION

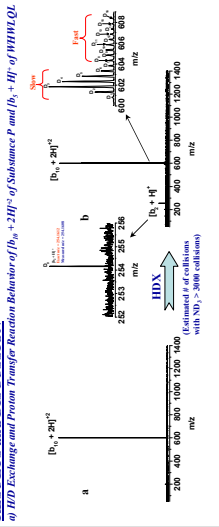


Figure 1: The mass spectrum of [B_n + 2H]⁺ (B_n = 2H⁺) of substance P after (a) 0 s reaction time with N₂ and (b) 0.500 s reaction time with N₂ at P(N₂) = 2.1 × 10⁻⁶ Torr. Note: [B_n + H]⁺ fragment does not exchange any one of the 6 labile hydrogens while [B_n + 2H]⁺ exchanges 18 out of the 20 labile hydrogens in the same reaction time.

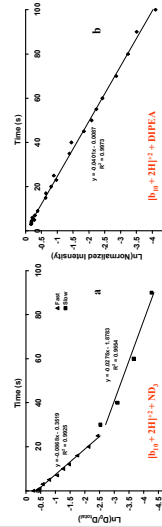


Figure 2: The temporal plot for (a) disappearance of [B_n + 2H]⁺ and (b) appearance of [B_n + H]⁺ in reaction with N₂ at P(DPEEA) = 1.8 × 10⁻⁶ Torr. Note: HDX exchange results yields that two populations while proton transfer reactions with DPEEA suggests the neutral B_n fragments are lower than P₁(N₂).

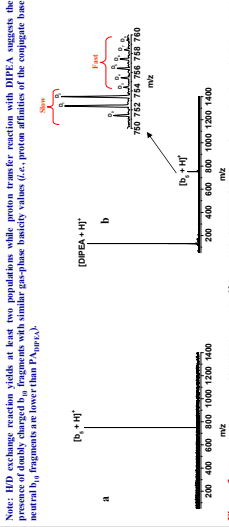


Figure 3: The mass spectrum of [B_n + H]⁺ after (a) 0 s reaction time with N₂ and (b) 0.500 s reaction time with N₂ at P(N₂) = 1.8 × 10⁻⁶ Torr in the presence of diisopropylamine (DIPA) (left over in the sample reservoir). Note: Figure 3b qualitatively shows that in the presence of DPEEA the first HDX exchanging population of B_n remains intact.

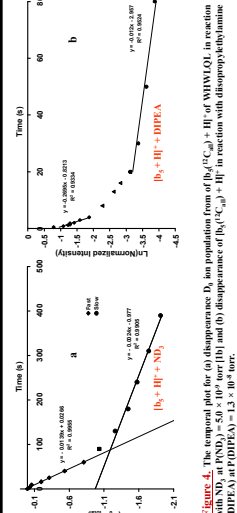


Figure 4: The temporal plot for (a) disappearance of [B_n + 2H]⁺ and (b) appearance of [B_n + H]⁺ in reaction with N₂ at P(N₂) = 5.0 × 10⁻⁶ Torr (b) and (c) disappearance of [B_n + 2H]⁺ in reaction with diisopropylamine (DIPA) at P(DIPA) = 1.3 × 10⁻⁶ Torr. Note: HDX exchange reaction yields two populations and proton transfer reaction DPEEA shows the presence of at least two different populations of singly charged B_n fragment ions.

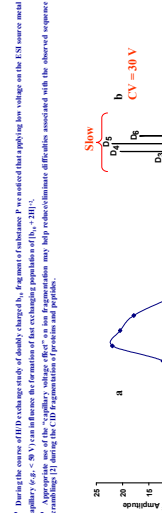


Figure 5: Capillary voltage (CV) effect on the amplitude and appearance/disappearance of first HDX exchanging population (CV = 30 V, 300 s reaction time with N₂ at P(N₂) = 1.4 × 10⁻⁶ Torr, (C) CV = 50 V, 300 s reaction time with N₂ at P(N₂) = 1.7 × 10⁻⁶ Torr, and (D) CV = 60 V, 300 s reaction time with N₂ at P(N₂) = 1.7 × 10⁻⁶ Torr.

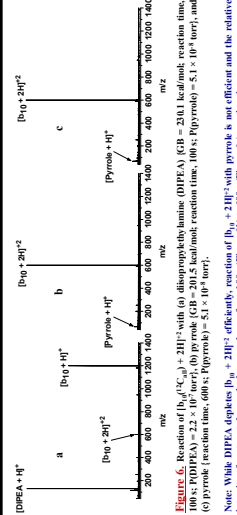


Figure 6: Reaction of [B_n + 2H]⁺ with (a) diisopropylamine (DIPA), (b) DPEEA, and (c) pyrolic ions. Note: While DPEEA replaces [B_n + 2H]⁺ efficiently, reaction of [B_n + 2H]⁺ with pyrolic is not efficient and the relative intensity of protonated pyrolic does not change from 100 s (Figure 6b) to 600 s (Figure 6c) reaction time.

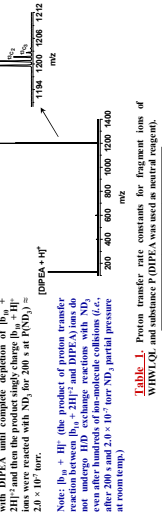


Figure 7: Proton transfer reaction of [B_n + 2H]⁺ followed by HD exchange reaction. Note: [B_n + 2H]⁺ reaction with ND₃ was isolated and reacted with DPEEA. The relative intensity of [B_n + 2H]⁺ fragment ions was 100% at P(ND₃) = 2.0 × 10⁻⁶ Torr.

Table 1: Proton transfer rate constants for fragment ions of WHWLQI and substance P (DPEEA was used as neutral reagent).

Fragment	[B _n + H] ⁺ (observed)	[B _n + 2H] ⁺ (observed P)	k ₁ = 2.3 × 10 ¹⁰ (cm ³ Mol ⁻¹ s ⁻¹)	k ₂ = 4.5 × 10 ¹⁰ (cm ³ Mol ⁻¹ s ⁻¹)
WHWLQI	1.5 × 10 ¹⁰	1.5 × 10 ¹⁰	1.5 × 10 ¹⁰	1.5 × 10 ¹⁰
Substance P	1.5 × 10 ¹⁰	1.5 × 10 ¹⁰	1.5 × 10 ¹⁰	1.5 × 10 ¹⁰

CONCLUSIONS
Proton transfer reactions between doubly charged B_n fragments and substance P with DPEEA (neutral reagent) did not create the two observed populations for reaction times less than 100 s. The two populations were observed after 100 s reaction time. The two populations were observed after 100 s reaction time. The two populations were observed after 100 s reaction time.

ACKNOWLEDGEMENTS
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