

Supporting Information for:

Ping-Pong Protons: How Hydrogen Bonding Networks Facilitate Heterolytic Bond Cleavages in Peptide Radical Cations

Konstantin O. Zhurov,¹ Matthew D. Wodrich,^{1,2} Clémence Corminboeuf,²

Yury O. Tsybin^{1}*

¹Biomolecular Mass Spectrometry Laboratory, Ecole Polytechnique Fédérale de
Lausanne, 1015 Lausanne, Switzerland

²Laboratory for Computational Molecular Design, Ecole Polytechnique Fédérale
de Lausanne, 1015 Lausanne, Switzerland

Table S1. Energies of relevant species. Absolute electronic energies, computed at the ω B97X-D/6-31G(d) level, given in hartree. Relative energies (in comparison to first transition state barrier height) given in kcal/mol.

Species	Electronic Energy	Relative Energy
Figure 1		
c4/z2 Cleavage TS	-1734.104771	0.00
c4/z2 Cleavage Products	-1734.126637	-13.72
Figure2		
c4/z2 Cleavage TS	-1734.128694	0.00
c4/z2 Cleavage Products	-1734.146870	-11.41
1 st Proton Transfer TS	-1734.145986	-10.85
1 st Proton Transfer Products	-1734.148541	-12.45
Figure 3		
c3/z3 Cleavage TS	-1734.127586	0.00
c3/z3 Cleavage Products	-1734.128318	-0.46
1 st Proton Transfer TS (H44 to O32)	-1734.127159	0.27
1 st Proton Transfer Products	-1734.137502	-6.22
Figure 4		
c3/z3 Cleavage TS	-1734.078510	0.00
c3/z3 Cleavage Products	-1734.093216	-9.23
1 st Proton Transfer TS (H3 to O12)	-1734.089965	-7.19
1 st Proton Transfer Products	-1734.095743	-10.81
2 nd Proton Transfer TS (H14 to O22)	-1734.086236	-4.85
2 nd Proton Transfer Products	-1734.091955	-8.44
3 rd Proton Transfer TS (H24 to O32)	-1734.088383	-6.20
3 rd Proton Transfer Products	-1734.099397	-13.11
Figure 5		
c2/z2 Cleavage TS	-1239.574084	0.00
c2/z2 Cleavage Products	-1239.596992	-14.37
1 st Proton Transfer TS (H4 to O38)	-1239.596836	-14.28
1 st Proton Transfer Products	-1239.636658	-39.27
Figure 6		
c3/z2 Cleavage TS	-1486.80329	0.00
c3/z2 Cleavage Products	-1486.849489	-28.99
1 st Proton Transfer TS (H44 to N33)	-1486.839048	-22.44
1 st Proton Transfer Products	-1486.852781	-31.06
Figure 7		
c3/z2 Cleavage TS	-1486.826299	0.00
c3/z2 Cleavage Products	-1486.850009	-14.88
1 st Proton Transfer TS (H3 to O12)	-1486.845132	-11.82
1 st Proton Transfer Products	-1486.851214	-15.63
2 nd Proton Transfer TS (H14 to O49)	-1486.844601	-11.48
2 nd Proton Transfer Products	-1486.854263	-17.55