

Supplementary Information for “Hydrogen migration reactions via low internal energy pathways in aminobenzoic acid dications”

Onni Veteläinen,^{*,†} Morsal Babayan,[†] Lassi Pihlava,[‡] Abdul Rahman Abid,[†] Antti Kivimäki,[¶] Edwin Kukk,[‡] Noelle Walsh,[¶] Samuli Urpelainen,[†] Olle Björneholm,[§] Marko Huttula,[†] Matti Alatalo,[†] Minna Patanen,[†] and Sergio Díaz-Tendero^{*,||, #}

[†]*Nano and Molecular Systems Research Unit, Faculty of Science, P.O. Box 3000, 90014 University of Oulu, Finland*

[‡]*Department of Physics and Astronomy, 20014 University of Turku, Finland*

[¶]*MAX IV Laboratory, Lund University, 22100 Lund, Sweden*

[§]*Department of Physics and Astronomy, Uppsala University, Box 516, 751 20 Uppsala, Sweden*

^{||}*Departamento de Química, Módulo 13, Universidad Autónoma de Madrid, 28049, Madrid, Spain*

[⊥]*Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, 28049, Madrid, Spain*

[#]*Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, 28049, Madrid, Spain*

E-mail: onni.vetelainen@oulu.fi; sergio.diaztendero@uam.es

Extended experimental details

The coincidence data was collected during two different experimental campaigns, and both times, the C 1s PEPICO spectrum of oABA was collected to confirm reproducibility. The reader is referred to a paper by Kooser *et al.*¹ for details of the TOF spectrometer and the gas-phase end station. During the first campaign, when the C 1s PEPICO spectra of mABA and oABA were measured, a higher extraction field (~ 13 kV/m) was applied in the TOF spectrometer,² and during the second campaign, when the C1s PEPICO spectra of oABA and pABA and the AEPICO spectrum of oABA were measured, we used a slightly lower extraction field (~ 10 kV/m). This leads to different TOFs of ions, but also some differences arise in how ions with high kinetic energy are collected, typically manifesting in the shape of the peaks.

The lower field settings were used in acquisition of the oABA AEPICO spectrum, achieved by setting aperture electrodes, separated by 30 mm, to +150 V and -150 V, respectively. The drift tube was set at potential of -935 V. The TOF spectrometer also has an aperture electrode for momentum imaging purposes, but being close to the extractor grid, it was set at -175 V, as we did not use the momentum imaging capabilities.¹ It should be noted that the use of a pulsed extraction field prevents the detection of H^+ ions, as the noise from the rising edge of the extraction field makes a low TOF region unusable, and is gated away.

Results of the molecular dynamics simulations

Simulations were performed for two rotamers of oABA and mABA: oABA1 and mABA1 refer to the lower energy rotamers with the C=O group pointing towards the NH_2 group, and oABA2 and mABA2 have the OH group closer to the NH_2 group. The results of the ADMP simulations with 10, 20 and 30 eV internal energies are summarized in Tables S1, S2 and S3 respectively. The total number of trajectories computed for each isomer at each energy was 1024. The propagation time for each trajectory was 250 fs. Only oABA2 produces

more H_3O^+ and H_2O compared to the other isomers, but oABA2 is not expected to be found in the sample at the experimental temperature, due to the energy difference compared to oABA1. We also see that at 10 eV internal energy the majority of trajectories remain unfragmented. This is most likely due to the insufficient propagation time of 250 fs, which is orders of magnitude shorter than the experimental flight times of the cations before reaching the detector. However, longer propagation times were deemed practically unfeasible for a large number of trajectories. The internal energies of 20 and 30 eV where the trajectories start to produce fragments belong to the regions II and III of the Auger electron spectrum (see figure 1 in the main text), which are not the regions of interest for our purposes (but the region I is). In this sense the molecular dynamics simulations are useful in describing the differences in fragmentation patterns between the isomers only qualitatively. By comparing the overall fragmentation after C 1s ionisation presented in fig. 2 of the main text and the results of 30 eV internal energy simulation, it can be seen that the simulations can reproduce some of the observed fragments. For example, the doubly charged parent ion $\text{C}_7\text{H}_7\text{NO}_2^{2+}$ at $m/z = 68.6$ is observed for all isomers, as well as $\text{C}_7\text{H}_5\text{NO}^{2+}$ ($m/z = 59.6$) for oABA and mABA. However, for example instead of the predicted $\text{C}_6\text{H}_7\text{N}^{2+}$ fragment, $\text{C}_6\text{H}_5\text{N}^{2+}$ ($m/z = 45.6$) is observed. From singly charged species, the predicted CHO_2^+ ($m/z = 45$) and $\text{C}_6\text{H}_6\text{N}^+$ ($m/z = 92.1$) fragments are observed in the mass spectra, but the simulations fail to predict significant amounts of smaller fragments below $m/z = 45$ which are detected in the experiment as well as some of the heavier ring-containing fragments. This could originate from the restricted simulation time and number of trajectories that we were able to simulate. It is reasonable to expect that more fragments could have appeared if the simulations had been extended.

Table S1: A frequency distribution of all fragmentation channels after simulating 1024 trajectories at 10 eV internal energy.

Channels	oABA1	oABA2	mABA1	mABA2	pABA
$\text{H}_3\text{O}^+ + \text{C}_7\text{H}_4\text{NO}^+$	-	1	-	-	-
$\text{H}_2\text{O} + \text{C}_7\text{H}_5\text{NO}^{2+}$	-	91	-	-	-
$\text{CO}_2 + \text{C}_6\text{H}_7\text{N}^{2+}$	-	-	1	-	1
$\text{CO} + \text{C}_6\text{H}_7\text{NO}^{2+}$	-	-	-	-	2
$\text{CHO}_2^+ + \text{C}_6\text{H}_6\text{N}^+$	2	3	21	7	19
$\text{C}_7\text{H}_7\text{NO}_2^{2+}$	1022	929	1002	1017	1002

Table S2: Counts of H_3O^+ and the most prominent fragments observed in trajectories at 20 eV of internal energy.

Fragments	oABA1	oABA2	mABA1	mABA2	pABA
H_3O^+	2	5	1	-	-
H_2O	40	200	16	31	9
$\text{C}_7\text{H}_5\text{NO}^{2+}$	39	186	14	29	8
CHO_2^+	255	232	315	331	265
$\text{C}_6\text{H}_6\text{N}^+$	253	231	312	324	263
$\text{C}_6\text{H}_7\text{N}^{2+}$	26	17	37	20	21
CO_2	27	19	39	22	21
CO	3	14	3	3	10
$\text{C}_7\text{H}_7\text{NO}_2^{2+}$	686	559	646	626	710

Table S3: Counts of H_3O^+ and the most prominent fragments observed in trajectories at 30 eV of internal energy.

Fragments	oABA1	oABA2	mABA1	mABA2	pABA
H_3O^+	2	12	5	4	4
H_2O	73	209	91	127	71
$\text{C}_7\text{H}_5\text{NO}_2^{2+}$	35	89	53	63	39
CHO_2^+	481	312	353	419	201
$\text{C}_6\text{H}_6\text{N}^+$	336	238	241	265	274
$\text{C}_6\text{H}_7\text{N}^{2+}$	52	39	55	46	45
CO_2	120	97	156	120	148
CO	28	78	47	60	41
H	58	57	44	37	63
H^+	94	115	84	67	125
H_2	169	104	101	99	159
NH_3	2	10	6	4	5
NH_3^+	2	7	1	-	1
CHN	21	28	58	57	34
$\text{C}_7\text{H}_5\text{NO}_2^{2+}$	44	33	21	20	40
$\text{C}_7\text{H}_6\text{NO}_2^+$	47	54	36	29	52
$\text{C}_7\text{H}_6\text{NO}_2^{2+}$	20	28	17	9	19
$\text{C}_7\text{H}_7\text{NO}_2^{2+}$	151	187	215	185	168

Auger profiles for selected fragments

Figure S1 shows high kinetic energy part of C 1s Auger spectra of electrons detected in coincidence with some selected relevant fragments discussed in the main text. The profiles are obtained from the coincidence map presented in fig. 3 of the main text by selecting a time-of-flight range and presenting an electron kinetic energy spectrum of electrons arriving in coincidence with ions in that range.

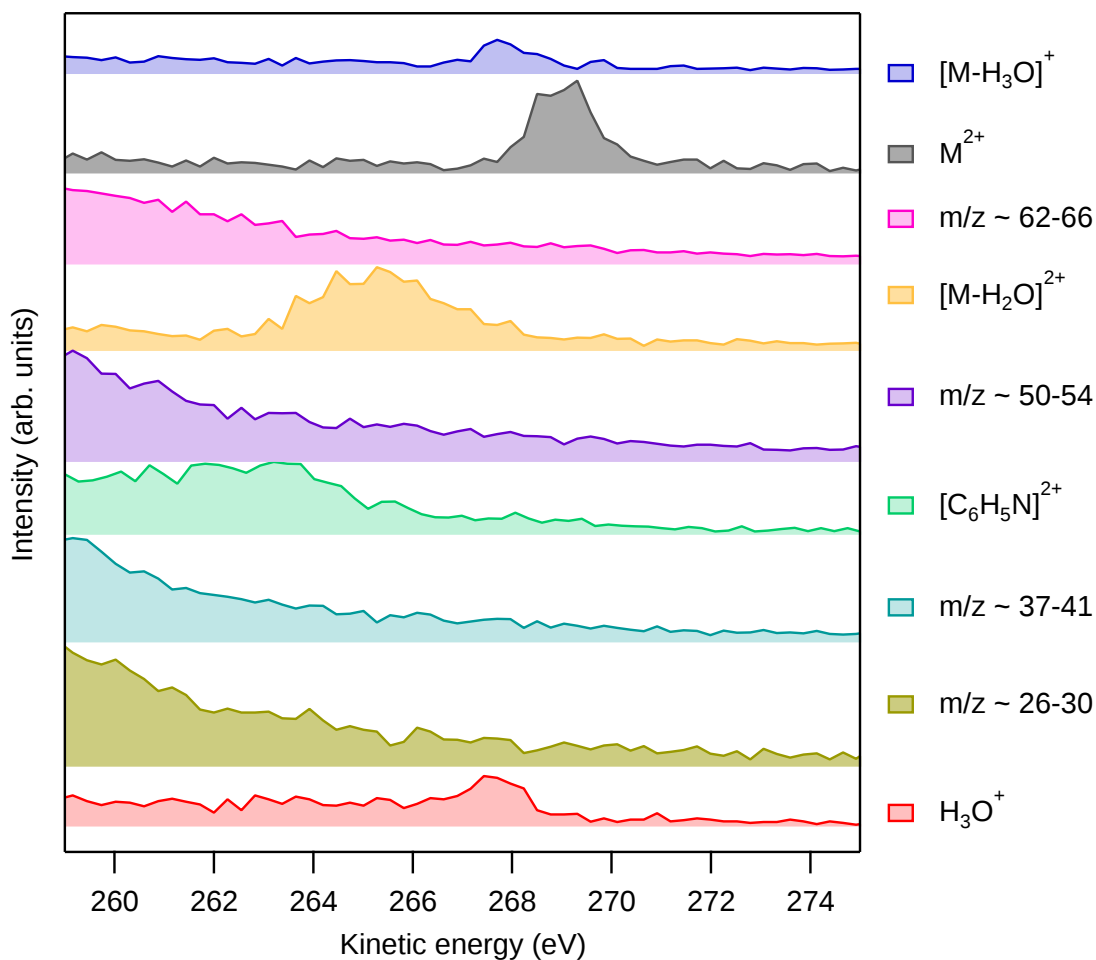


Figure S1: High kinetic energy part of C 1s Auger spectrum profiles of electrons detected in coincidence with some observed fragments. The profiles have been offset and scaled in y-axis for better visibility.

Partial charge analysis and microcanonical rate coefficients

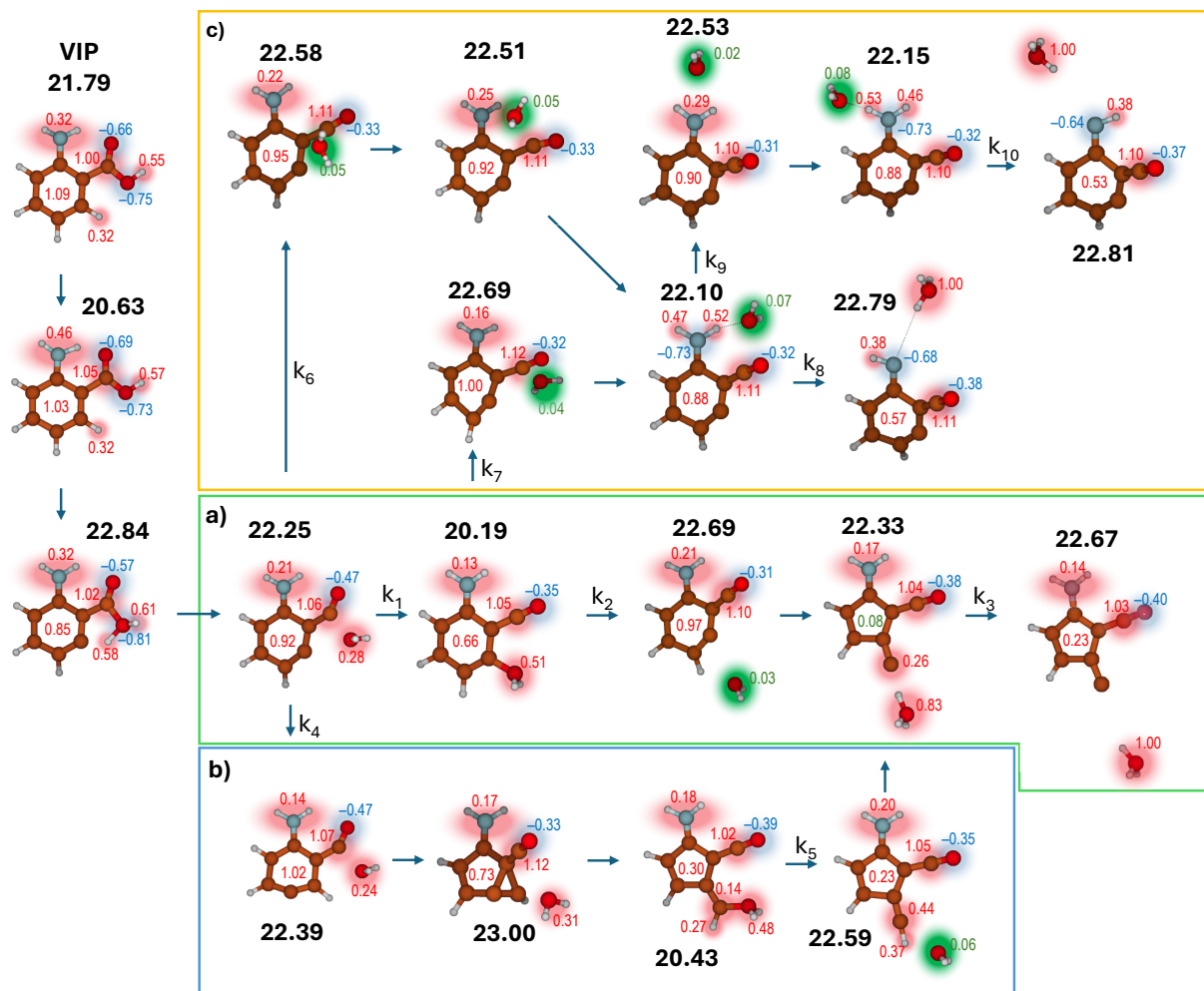


Figure S2: Natural bond orbital (NBO) analysis^{3,4} of some structures from Figure 4 of the main text. Red and blue shadows indicate positively and negatively charged areas, respectively, while green shadows indicate neutral areas. The remaining total charge of unshaded areas is reported in the middle of the ring for each structure. The structures are identified by their energy levels (in eV, including zero-point corrections and relative to the neutral ground state, as in Figure 4). Arrows at major energetic barriers or branching points are labeled with their corresponding rate coefficients k , which are reported in table S4.

Figure S2 shows the results of NBO partial charge analysis on some key structures of the fragmentation pathways presented in Figure 4 of the main text. The structures depicted Figure S2 a), b) and c) correspond to the pathways depicted in Figure 4 a), b), and c),

respectively. As discussed in the ‘Results and discussion’ section of the main text, all the pathways begin with the migration of a hydrogen from the ring to the carboxyl group, leading to formation of a neutral water fragment, which may after a roaming period abstract a proton from the parent ion to produce H_3O^+ . The partial charge analysis confirms the neutrality of the roaming H_2O and the charge transfer from the parent to the H_3O^+ ion at the final transition states of each pathway. In pathways a) and b) the H_2O reattaches to the ring before re-emission and proton abstraction. The proton in these pathways is taken from the ring and therefore the ring structure is ultimately left with a close to neutral charge. This appears to be associated with the transformation into the five-membered ring structure which does not happen in the pathways presented in c). In the pathways presented in c), the proton is taken from the $-\text{NH}_2$ group and the loss of charge is shared between the functional group and the ring, and this seems to preserve the benzene structure. The charge distribution on the $-\text{CO}$ group is mostly unaffected by the processes subsequent to its formation, being nearly equivalent in all three final transition states.

Table S4: The microcanonical rate coefficients (Hz) of the fragmentation pathways. The rate coefficients were calculated for the transition states with the highest energy barriers or ones at important branching points. See the labeled arrows in Figure S2 for the these processes.

Rate coefficient (Hz)	k_1	k_2	k_3	k_4	k_5
	8.15×10^{12}	6.65×10^5	1.31×10^{13}	8.86×10^5	7.54×10^7
Rate coefficient (Hz)	k_6	k_7	k_8	k_9	k_{10}
	1.95×10^{12}	7.44×10^6	7.43×10^{11}	1.60×10^{11}	9.43×10^{12}

The microcanonical rate coefficients in Table S4 were calculated according to microcanonical transition state theory as⁵

$$k(E) = \frac{W^\ddagger(E)}{h\rho(E)}, \quad (1)$$

where $\rho(E)$ is the density of states of the initial (minimum) structure at energy E , $W^\ddagger(E)$ is the integrated density of states of the transition state up to the energy E , and h Planck’s

constant. The density of states was calculated within the harmonic approximation as:⁶

$$\rho(E) = \frac{E^{f-1}}{\Gamma(f) \prod_{i=1}^f (h\nu_i)}, \quad (2)$$

where f is the number of vibrational degrees of freedom of the structure, ν_i the frequencies of its vibrational modes and Γ is Euler’s gamma function. For the calculation of the rate coefficients we take the total energy of the system to be the sum of three components: the energy of the VIP structure (21.79 eV), the excitation energy from the Auger process (1.2 eV, being the energy where the H_3O^+ fragment is observed, see main text) and the thermal vibrational energy of the neutral molecule at the experimental temperature according to the canonical thermochemical analysis as implemented in Gaussian16⁷ (3.8 eV). We can see in Figure S2 the first branching point of the three pathways that k_4 is many orders of magnitude smaller than k_1 and k_6 (leading to pathways a) and c), respectively) and therefore we expect b) to be by far the least likely of the three pathways. The fragmentation process then proceeds towards pathways a) and c) by the roughly equal rate coefficients k_1 and k_6 . However at the next branching point in a) the process is driven towards pathway c), since k_7 is considerably larger than k_2 . The coefficients k_8 , k_9 and k_{10} are all very large, so once the system reaches either of the initial structures in c), the system should proceed efficiently towards the production of H_3O^+ .

References

- (1) Kooser, K.; Kivimäki, A.; Turunen, P.; Pärna, R.; Reisberg, L.; Kirm, M.; Valden, M.; Huttula, M.; Kukk, E. Gas-phase endstation of electron, ion and coincidence spectroscopies for diluted samples at the FinEstBeAMS beamline of the MAXIV 1.5 GeV storage ring. *Journal of Synchrotron Radiation* **2020**, *27*, 1080–1091.
- (2) Abid, A. R.; Veteläinen, O.; Boudjemia, N.; Pelimanni, E.; Kivimäki, A.; Alatalo, M.;

- Huttula, M.; Björneholm, O.; Patanen, M. Forming Bonds While Breaking Old Ones: Isomer-Dependent Formation of H_3O^+ from Aminobenzoic Acid During X-ray-Induced Fragmentation. The Journal of Physical Chemistry A **2023**, 127, 1395–1401, PMID: 36749682.
- (3) Foster, J. P.; Weinhold, F. Natural hybrid orbitals. Journal of the American Chemical Society **1980**, 102, 7211–7218.
- (4) Reed, A. E.; Weinhold, F. Natural bond orbital analysis of near-Hartree–Fock water dimer. The Journal of Chemical Physics **1983**, 78, 4066–4073.
- (5) Forst, W., Ed. Theory of Unimolecular Reactions; Physical Chemistry; Elsevier, 1973.
- (6) Aguirre, N. F.; Díaz-Tendero, S.; Hervieux, P.-A.; Alcamí, M.; Martín, F. M3C: A Computational Approach To Describe Statistical Fragmentation of Excited Molecules and Clusters. Journal of Chemical Theory and Computation **2017**, 13, 992–1009.
- (7) Frisch, M. J. et al. Gaussian 16 Revision C.02. 2016; Gaussian Inc. Wallingford CT.