Mechanistic insight into the kinetic fragmentation of Norpinonic Acid in the gas phase: An experimental and DFT study

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Abstract. Norpinonic acid has been known as an important α-pinene athmospheric SOA (Secondary Organic Aerosol) component. It is formed in the reaction of α-pinene, β-pinene or verbenone with atmospheric oxidizing reagents, such as ozone

10 (O3) and hydroxy radicals. In the presented studies, tandem mass spectrometry techniques were used to determine the exact norpinonic acid fragmentation pathway in the gas phase. The precursor anion – deprotonated norpinonic acid (m/z 169) generated in an electrospray (ESI) source were subjected into the collision cell of the mass spectrometer and fragmented using CIE (Energy-Resolved Collision Induced Dissociation) technique. Based on the analysis of the breakdown curves, the experimental energy values required to initiate the gas - phase degradation processes were determined. Quantum chemical

15 calculations of the reaction models for observed fragmentation processes were also constructed, including calculation of all transition states presented in the reaction mechanism. Comparison between the experimental and the theoretical threshold energies calculated at ωB97XD/6-311+G(2d,p) level of theory has shown a very good correlation. Two basic pathways of the fragmentation of the parent anion [M-H]⁻ (m/z 169) were observed. A first, lead to the decarboxylation product (m/z 125) and second to the loss of neutral molecule (C_4H_6O) together with the formation of anion m/z 99. Loss of C_3H_6 or C_2H_4O molecules

20 and formation of the anion m/z 41, together with anion m/z 55, were found for fragment anion m/z 99. Further breaks down of anion m/z 125 give a rise of 69, 57 and 55 m/z ions. To confirm structures formed during ER-CID experiments, the gas-phase proton transfer reactions were examined of all Norpinonic acid anionic fragments with a series of neutral reagents, characterized by different Proton Affinity (PA) values. It was found that only m/z 55 and m/z 69 anionic fragmentation products have higher PA values and accept the proton from all neutral reagents. Based on PA differences analysis, the most

25 possible chemical structures were proposed for the observed fragment anions.

1 Introduction

Earth's atmosphere contains a tremendous amount of organic compounds, which differ in fundamental properties such as, volatility, reactivity, hygroscopicity and propensity to form cloud droplets (Hallquist et al., 2009). It is estimated that 10 000 to 100 000 different organic compounds have been measured in the atmosphere (Goldstein, 2007). Organic aerosols are emitted

30 to the atmosphere directly from a wide variety of natural and anthropogenic sources (Hallquist et al., 2009). Globally, about 1300 Tg of volatile organic compounds (VOC) are emitted each year to the atmosphere, from a biomass burning, combustion

of fossil fuels, volcanic eruptions, vegetation processes (Olsson and Benner, 1999; Seinfeld and Pandis, 2016). The chemical reactions of volatile organic compounds (VOCs) with different atmospheric oxidizing reagents, such as ozone (O_3), •OH radicals and •NO_3 radicals result with secondary organic aerosol (SOA) formation (George and Abbatt, 2010; Gómez-González

35   et al., 2012; Kavouras et al., 1999).

Studies on the chemical composition of SOA have reported the formation of a number of multifunctional products, among which, compounds with carboxylic functional groups are observed in large amount. Due to their low volatility, mono, di- and tricarboxylic acids have been also suggested as key species in gas-to-particle conversion processes (Christoffersen et al., 1998; Glasius et al., 2000; E. Jenkin et al., 2000; Claeys et al., 2007).

40   Field studies have shown that few organic acids formed during α-pinene oxidation process, such as pinic acid, pinonic acid, norpinic acid, norpinonic acid and their isomers, are prominent components of atmospheric aerosol natural samples (Lignell et al., 2013; Feltracco et al., 2018; Pathak et al., 2007; Kavouras et al., 1998).

The analytical toolbox available for chemists to study atmospheric organic components has expanded considerably during the past decades (Hallquist et al., 2009). A wide variety of analytical techniques are used to the structural characterization of

45   organic aerosol (OA) products, e.g., gas chromatography/mass spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS), nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy (Takahama et al., 2016; Zanca et al., 2017; Finessi et al., 2012). In particular, liquid chromatography in combination with high-resolution negative ion electrospray ionization mass spectrometry is widely used to identificate and the quantificate the atmospheric aerosol polar and organic components (Gómez-González et al., 2012). Identification is mostly based on second-order mass

50   spectra (MS/MS), which together with an elemental composition of target ion signals obtained from high-resolution measurements helps with the structural characterization of the organic compounds (Szmigielski et al., 2007; Claeys et al., 2009; Kourtchev et al., 2008). However, to the proper identification of OA components, mentioned MS/MS measurements should be made very accurately, to have full confidence with the organic compound structural characterization during the field or ambient samples analytical process.

55   In this publication, we have focused on one of the α-pinene SOA component - Norpinonic acid, which is formed in the reaction of α-pinene with atmospheric oxidizing reagents, such as ozone (O_3) or OH radicals (Zhang, 2015; Ma et al., 2008; Winterhalter et al., 2003; Ma et al., 2007; Peeters et al., 2001). Reported concentration of Norpinonic acid in the atmosphere is considerable significant about 0.2 – 1.1 ng·m^{-3} (Li et al., 2013). It is known, that the majority of the chemical process in the atmosphere are induced by the radical species both in the night and day times. However, it is also proposed that some of the chemical

60   transformations in the atmosphere may proceeds *via* other chemical routes that do not require the presence of radicals, which might go through anionic or cationic pathways e.g. the ion cluster formation or deprotonation of acidic structures by basic inorganic agents (Richards et al., 2020; Jarrold, 2023; Hirsikko et al., 2011; Mccrumb and Arnold, 1981; Krivácsy et al., 1997; Blanco-Heras et al., 2008). While, there are no models proposing intra or bimolecular reaction paths, e.g. the kinetic, or thermodynamic energy-induced degradation process that can break SOA or other organic and inorganic components into

65   fragments within ionic chemical transformations.

Herein, we studied the Norpinonic acid anionic fragmentation pathway in the gas phase, together with identification of the exact ion fragment structures based on the second-order mass spectrum (MS/MS) recorded during energy resolved collision-induced dissociation mass spectrometry experiments (ER-CID). Detailed analysis of recorded breakdown curves has been provided, which have led to the experimental energy values required to initiate of each gas-phase degradation processes. In addition, structural analysis have been made through the bimolecular reactions between Norpinonic acid anion and its anionic fragments were performed with a series of neutral reagents (CH$_3$SCN, CH$_3$SSCH$_3$, CHCl$_3$, CHBr$_3$, CH$_2$Cl$_2$, CH$_3$NO$_2$) to analyze the difference in Proton Affinity (PA) values based on observation of the proton-transfer reaction. Quantum chemical calculations of the reaction models for all observed fragmentation processes were also conducted, including determination of all transition states presented in the reaction mechanism. Expanding the knowledge about the structures of fragments formed during ER-CID-MS experiments lead to the better understanding potential reaction pathways of studied compounds in the atmosphere (Nozière et al., 2015).

2 Experimental section

2.1 General Materials and Methods

C*is*-norpinonic acid was synthesized in the Laboratory of the Environmental Chemistry in the Institute of Physical Chemistry PAS using an optimized synthetic procedure based on previously reported method by Moglioni et al. (Moglioni et al., 2000). A detailed synthetic procedure for the preparation and purification of the norpinonic acid along with the IR, ESI-HR-MS, ^{1}H and ^{13}C NMR analytical spectra of the final product are provided in Supporting Information.

2.2 Mass spectrometry experiments

All experiments were performed using a modified Micromass/Waters Q-ToF 2 spectrometer (Błaziak et al., 2017; Blaziak et al., 2018; Miller et al., 2014) equipped with electrospray (ESI) ion source operated in the negative ion mode. The norpinonic acid anion (*m/z* 169) was generated by introducing to the ESI source an aqueous – methanolic (2:1) solution of 1 mM Norpinonic acid using a syringe pump at a flow rate of 0.2 ml/min. The main fragmentation product ions investigated in this work were formed in two ways: upon collision activation in the collision cell by varying the collision kinetic ion energy and in the ion source by varying the capillary and cone voltages accelerating the in-source bond breaking process. For the energy resolved collision-induced dissociation (ER-CID) experiments argon (Ar) was used as collision gas, while for the bimolecular gas phase reactions different reagent vapors were introduced to the collision cell using an in-house gas inlet system (Błaziak et al., 2017; Blaziak et al., 2018; Miller et al., 2014). The bimolecular reactions together with proton affinity analyses were carried out to identify the isomeric and conformational diversity of the Norpinonic acid anionic fragments formed both in the collision cell and the ion source of the mass spectrometer. Volatile reagents introduced to the collision cell and used for the bimolecular reactions as neutral reagents were as follows: methyl thiocyanate, dimethyl disulfide, chloroform, bromoform, dichloromethane and nitromethane. In presented studies a full series of the breakdown curves were recorded to determine the

onset/threshold energies of the Norpinonic acid fragmentation reactions. Collision spectra were recorded by varying the collision energy in incremental steps with an energy resolution of 8–25 eV in the lab frame and 5-10 minutes of collection time at each step. To enable the comparison of the observed process a linear fit of the approximately linearly rising section of the breakdown curve was performed for each dataset. The onset energy has been defined at each gas pressure by calculation of the energy (X value) at zero intensity (Y = 0). Additionally, to compare the experimental and theoretical energy landscapes, the gas pressure linear extrapolation has been also performed. The onset energies defined at five different gas pressures were similarly linearly extrapolated to the zero pressure point, giving the final threshold energies reported in this work.

2.3 Quantum chemical calculation

All calculations were performed with Gaussian 09 suite of programs (M. J. Frisch, 2009). The Cartesian coordinates of the initial geometries were created using the GaussView 5.0 program (Dennington R., 2009). The geometries of the reactants, products, intermediates and transition states were optimized using CAM-B3LYP, PBE1PBE and ωB97XD functionals with the same 6-311+G(2d,p) basis set. No symmetry restrictions were used during the calculation. Harmonic frequencies were used to identify the ground state structures with all real frequencies and transition states (TS) with only one imaginary frequency. The IRC computations were also performed to ensure that each TS structure corresponds to the desired products and substrates. Zero-point energy (ZPE) corrections were included in energy calculations.

3 Results and discussion

3.1 Fragmentation pathway of Norpinonic acid an anion

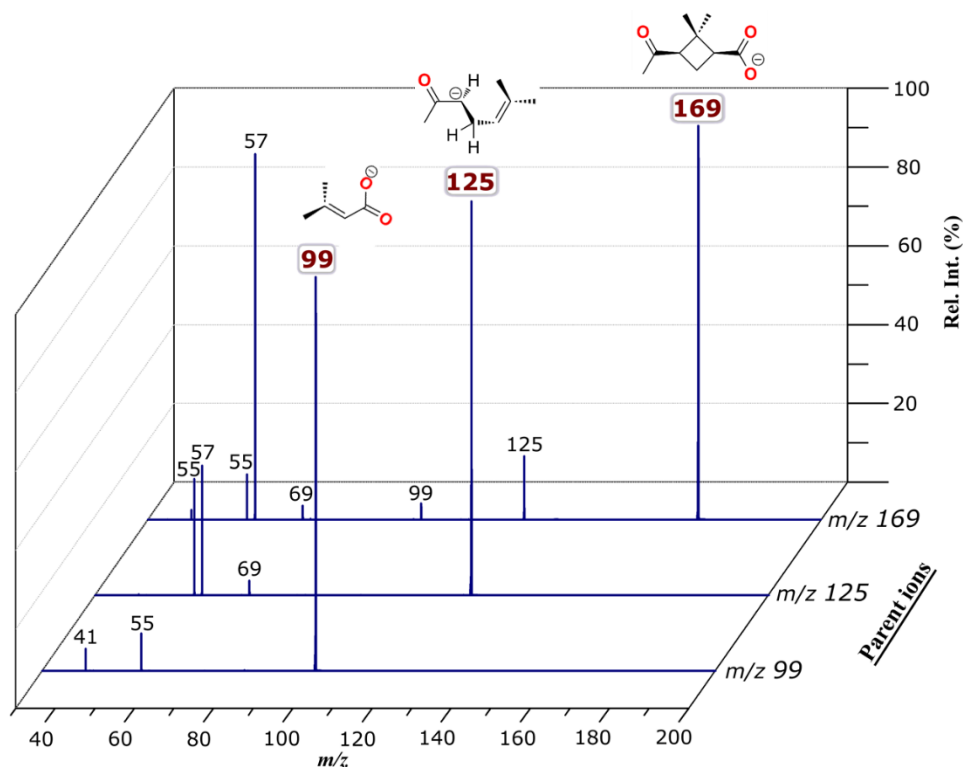
Introducing a methanolic-aqueous solution of the norpinonic acid to the electrospray ion source of the mass spectrometer gives a rise to deprotonated anion corresponding to $C_9H_{13}O_3^-$ (m/z 169) in the negative ion mode. Subjecting these ions to collisional activation leads to the formation of fragment ions, corresponding to $C_8H_{13}O^-$ (m/z 125), $C_5H_7O_2^-$ (m/z 99), $C_3H_5O^-$ (m/z 57), $C_4H_5O^-$ (m/z 69), $C_4H_7^-$ (m/z 55) and C_2HO^- (m/z 41) anions. Representative ER-CID mass spectra of $C_9H_{13}O_3^-$ (m/z 169) as well as for fragment ions (m/z 125 and m/z 99) taken at the center-of-mass collision energy ECM = 3.8 eV, 4.1 eV and 4.3 eV (CM), respectively, with argon collision gas at nominal pressures of 3.54 ×10-4 mBar are shown in Fig. 1.

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Figure 1. Fragment ion mass spectra of m/z 169, m/z 125 and m/z 99 recorded with a ToF voltage of 3kV, taken at a collision energy of 3.8 eV, 4.1 eV and 4.3 eV (ECM), respectively with argon collision gas at nominal pressures of 3.54 × 10-4 mBar.

Additionally, to analyze the energetic requirements for each observed fragmentation pathway, the full set of breakdown curves

125   for all of the ions have been recorded, by varying stepwise the kinetic collision energy in five different collision gas pressures.

The threshold energies were estimated by employing a simple extrapolation procedure, which in details has been described in

Supplementary Information (SI). Figure 2 shows the representative breakdown diagrams of m/z 169, m/z 125 and m/z 99

recorded with Ar collision gas at a nominal pressure of $1.06 \times 10{-4}$ mbar, $1.08 \times 10{-4}$ mbar, $1.06 \times 10{-4}$ mbar, respectively.

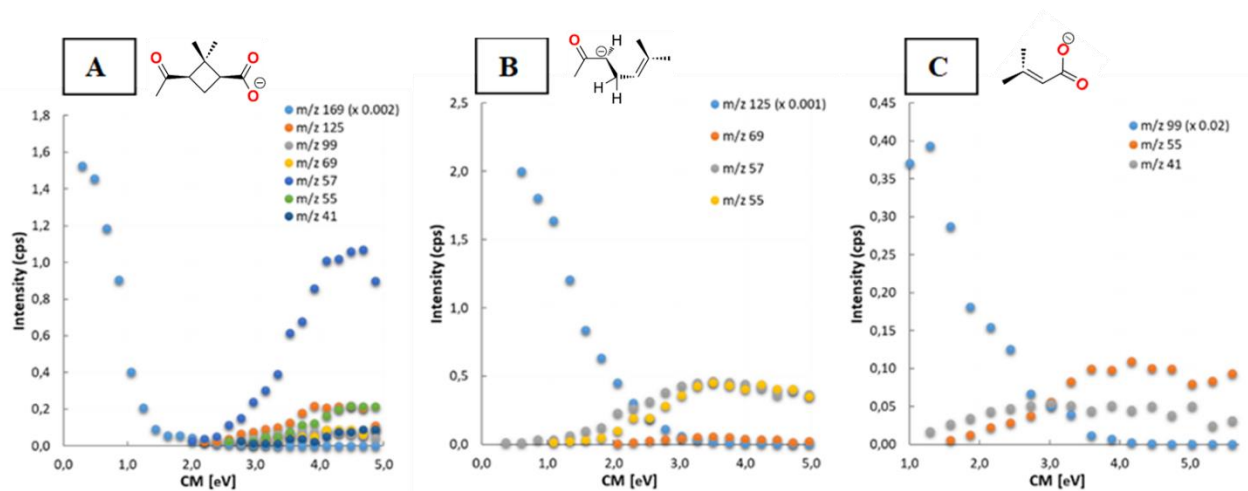
For other spectra, as well as for additional breakdown curves please consult the SI.

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Figure 2. Breakdown curves from the CID experiments on m/z 169 (A), m/z 125 (B) and m/z 99 (C) – with the ion intensity for the individual ions as a function of ECM. Please note the different scales of the ordinates. The data were recorded with Ar collision gas at a nominal pressure of 1.06×10^{-4} mbar, 1.08×10^{-4} mbar, 1.06×10^{-4} mbar, respectively.

The experimentally measured reaction energies and the general fragmentation network of the main m/z 169 Norpinonic acid

135   anion has been shown in Fig. 3.

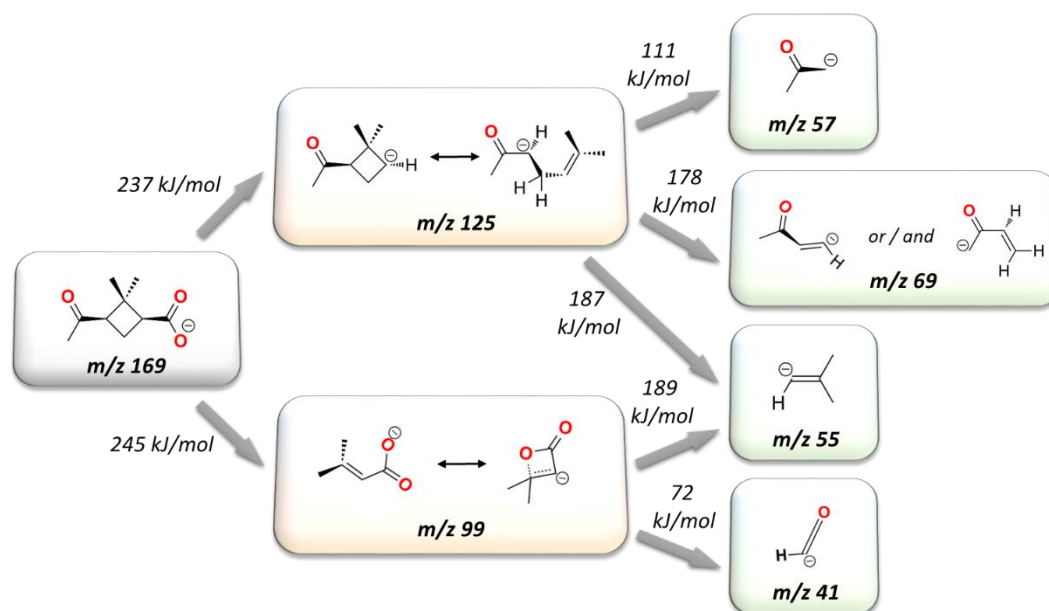



Figure 3. The fragmentation network for deprotonated norpinonic acid (m/z 169). Please note that above the gray arrows the experimental threshold energies (kJ/mol) for each fragmentation reaction are shown.

It was found that the parent anion $C_9H_{13}O_3^-$ (m/z 169) undergoes two main fragmentation pathways. The first is expressed by

140   the loss of neutral fragment C_4H_6O (mass 70), resulting in formation of $C_5H_7O_2^-$ (m/z 99) anion with an experimentally

established appearance energy of 237 (± 70) kJ/mol. The second, a decarboxylation reaction leading to $C_8H_{13}O^-$ (m/z 125), with onset energy at 245 (± 73) kJ/mol. In order to establish the detailed fragmentation network of the main anion, separate ER-CID experiments were performed for each smaller anionic fragments that were observed on main product-ion spectra. Consequently, on the ER-CID mass spectrum of m/z 99 two secondary fragmentation products have been observed. The

145 formation of C_2HO^- (m/z 41) followed by the loss of the neutral molecules C_3H_6O, with estimated fragmentation energy at 72 (± 22) kJ/mol. Anion $C_5H_7O_2^-$ (m/z 99) was also prone to loss carbon dioxide molecule, which leads to the formation of $C_4H_7^-$ (m/z 55) anion, at the energy of 189 (± 56) kJ/mol. The separate ER-CID experiment for m/z 125 anion has shown, that in-cell activation leads to three different fragmentation pathways. In the first route, the m/z 69 anion is formed by the loss of the neutral molecule C_4H_8 (mass 56), with an experimentally established appearance energy of 178 (± 53) kJ/mol. Second pathway,

150 leads to the formation of the anionic compound $C_3H_5O^-$ (m/z 57) and the loss off neutral molecule C_5H_8 (mass 68), with determined energy of 111 (± 33) kJ/mol. Finally, a third observed fragmentation pathway gives a rise to the mass signal corresponding to the $C_4H_7^-$ (m/z 55) anion followed by the formation of the neutral molecule C_4H_6O (mass 70). Extrapolation of the linearly rising section of the breakdown curve for m/z 55 gives an onset energy of 171 (± 51) kJ/mol for this process.

3.2 Structural analysis of observed ion fragments

155 Further insight into the observed fragmentation pathway of deprotonated Norpinonic acid (*m/z* 169) was obtained through quantum chemical calculations. In particular, we applied three different DFT methods – ωB97XD/6-311+G(2d,p), CAM-B3LYP/6-311+G(2d,p) and PBE1PBE/6-311+G(2d,p) to explore the energetic and conformational landscape of observed fragmentation processes. In general, all employed methods were found to describe properly the main experimental observations. We have chosen to highlight in the main text the results obtained with the ωB97XD hybrid density functional

160 since this method reproduces the experimental observation the most accurately (Chai and Head-Gordon, 2008). For the comparison the other theoretical results please consult the SI.

Reaction models for all observed fragmentation processes were computationally modeled, including determination of all possible transition states (TS) and alternative fragmentation pathways that forms the full reaction mechanism. The potential energy surface for the first main fragmentation pathway that leads through the $C_8H_{13}O^-$ (*m/z* 125) anion formation to other

165 smaller fragments, together with established chemical structures are shown in Fig. 4.

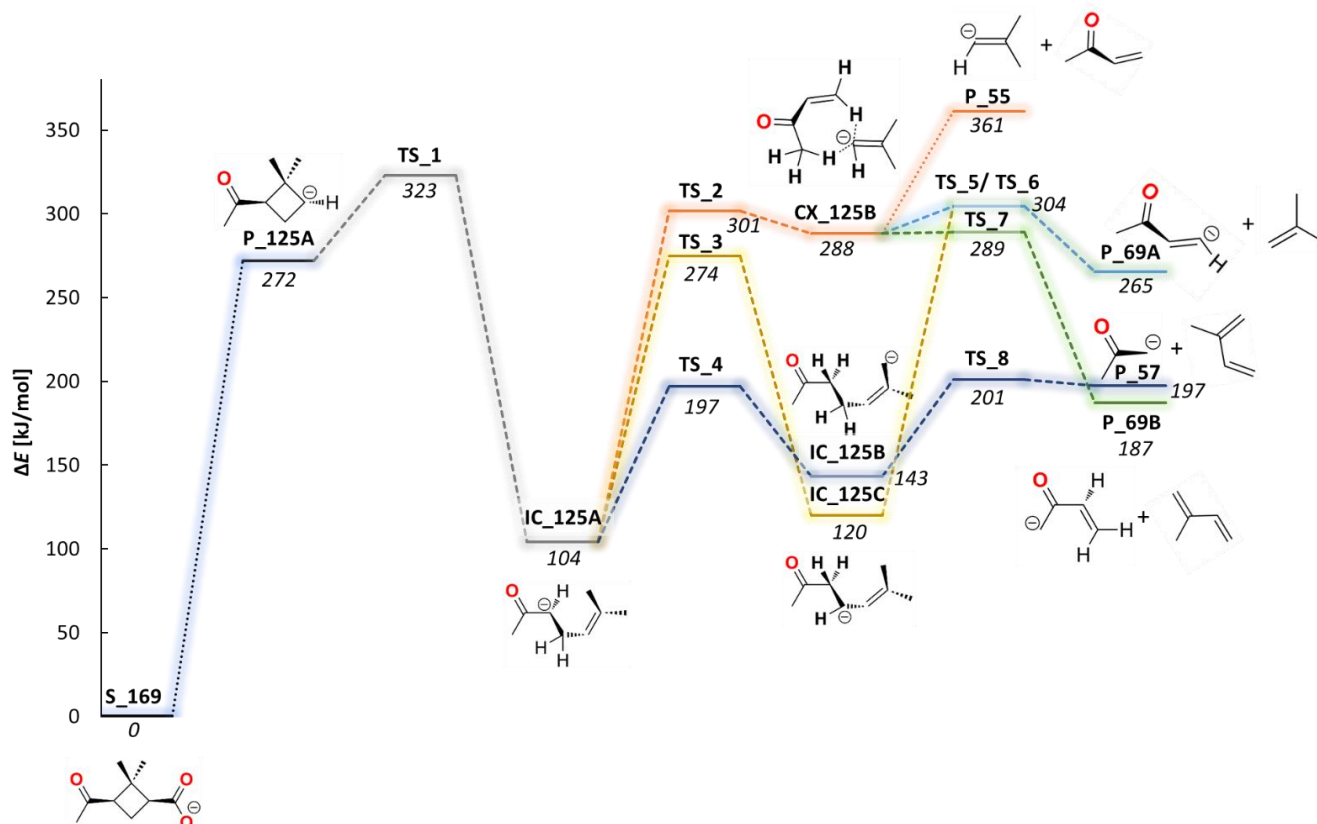



Figure 4. Computed potential energy (ωB97XD/6-311+G(2d,p)) diagrams describing first fragmentation pathway of m/z 169 ions via m/z 125 and further to smaller anionic fragments m/z 69, m/z 57, m/z 55. Abbreviations used in the structure names: S – Substrate, P – Product, TS – Transition State, IC– intermediate structure, and CX – intermediate complex.

170   Decarboxylation reaction of deprotonated Norpinonic acid $C_9H_{13}O_3^-$ (*m/z* 169) leads to the cyclic structure of *m/z* 125 (**P_125A**). Further DFT analysis of the fragmentation products anion *m/z* 125 has shown that **P_125A** is able to rearrange by the cleavage of four-membered carbon ring to the more thermodynamically stable "open" structure **IC_125A** *via* relatively low energy barrier **TS_1** at 58 kJ/mol above **P_125A** energy level. Interestingly, a similar breaking of a four-member ring had been formally reported earlier by Yasmeen, F. et al, where the fragmentation of Norpinic acid − as a product of oxidation

175   reaction of Norpinonic acid, has been discussed (Yasmeen et al., 2010). Notably, this observation has a fundamental impact on further mechanistic analysis and for understanding of the thermodynamic and kinetic nature of generated ions. While, *m/z* 125 ion is formed in the collision-cell of the mass spectrometer from the *m/z* 169 precursor ion (during the ER-CID experiments), by the precise dosing of the ion collision energy, the kinetically controlled product (**P_125A**) is formed. Due to this fact the excellent correlation between the experimental (245 (± 73) kJ/mol) and computed energies (272 kJ/mol) for

180   decarboxylation reaction of m/z 169 ion has been noted. On the other hand, to provide the quantitative energy measurements for consequent fragmentations reactions of smaller fragments, the initial in-source fragmentation of *m/z* 169 was performed. Due to thermodynamic conditions of the electrospray ionization and fragmentation processes in the ion source, the in-source

formed *m/z* 125 ions take more likely the "open" **IC_125A** isomeric form. Taking this into account, from this point the thermodynamic "open" isomer **IC_125A** start to play the reference role for sequent measurements. In this respect, further

185 collisional activation analysis of in-source formed *m/z* 125 ions has shown, that this anion undergoes three fragmentation pathways. Calculations of the first proposed fragmentation pathway of *m/z* 125 leads to *m/z* 55 anion *via* one transition state (**TS_2**) and intermediate structure **CX_125B**. It was found that anion $C_4H_7^-$ (*m/z* 55) is formed together with the neutral molecule C_4H_6O (mass 70), attributed to the methyl vinyl ketone (MVK) structure (**Pº_70**), placed 257 kJ/mol above the **IC_125A** energy level. The **CX_125B** intermediate complex can also undergo alternative transformation through a transition

190 state (**TS_5**) to anion *m/z* 69. Transition state energy (**TS_5**) was calculated to be 200 kJ/mol above **IC_125A** energy level. In this step of the reaction mechanism, the anion *m/z* 69 (**P_69A**) is formed, together with the neutral molecule C_4H_8 (mass 56), which corresponds to neutral molecule of 2-methylpropene chemical structure (**Pº_56**). On the other hand, the alternative mechanism for *m/z* 69 anion formation may lead to **P_69B** structure through different transition state (**TS_7**), which has lower energetic requirements. The energy of **TS_7** was calculated at 185 kJ/mol above **IC_125A** energy level. Third calculated

195 pathway leading to the formation of the anionic compound $C_3H_5O^-$ (*m/z* 57) by the loss of neutral fragment C_5H_8 (mass 68) corresponding to 2-metylobuta-1,3-dien structure, also known as isoprene (**Pº_68**). It was found that alternative transition state energies for the formation of two different *m/z* 57 anion isomers were calculated to be 197 kJ/mol and 201 kJ/mol, for **TS_4** and **TS_8**, respectively. Notably, the experimental appearance energy for *m/z* 57 formation estimated from the experiment (111 (± 33) kJ/mol) is slightly higher than the computed transition state energy values (85 kJ/mol).

200 The second part of the potential energy diagram calculated for the fragmentation pathway of main *m/z* 169 anion that leads through *m/z* 99 ion to smaller ion fragments *m/z* 41 and 51 formation is shown in Fig. 5.

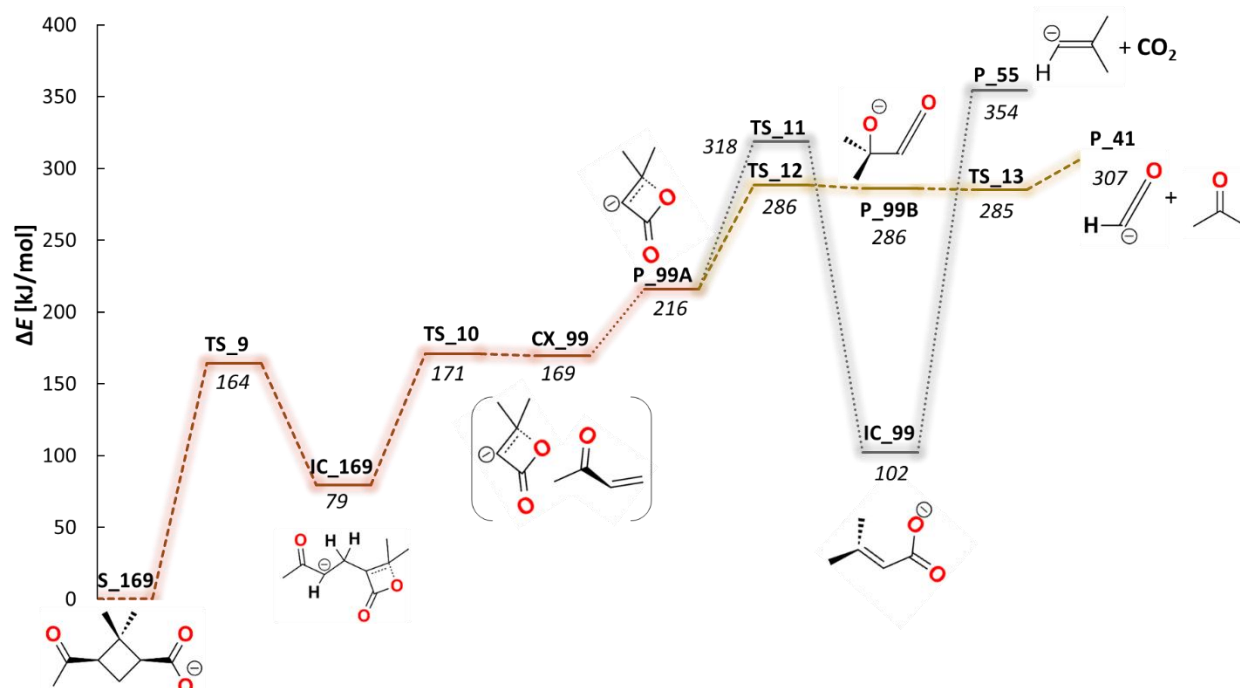



Figure 5. Computed potential energy (ωB97XD/6-311+G(2d,p)) diagrams describing second fragmentation pathway. Abbreviations used in the structure names: S – Substrate, P – Product, TS – Transition State, IC– intermediate structure, and CX – intermediate complex.

It has been shown that the primary fragmentation product *m/z* 99 anion can form two alternative isomeric structures, a first where anion is located on the carbon atom (**P_99A**) or second, where negative charge occurs on oxygen atom (**P_99B**). Structure **P_99A** is formed on exothermically way, that formally proceeds through two transition states **- TS_9** and **TS_10** and two intermediate mechanistic point, intermediate structure **IC_169** and complex **CX_99** with the ultimate reaction energy for **P_99A** calculated at 216 kJ/mol. This part of the mechanism can be referred to the kinetic ER-CID experimental results with estimated energy for *m/z* 99 ion formation at 245 kJ/mol. Based on the computed chemical transformations of the m/z 99 ion it is seen that the more thermodynamically stable isomer **P_99B** can be formed *via* opening of lactone ring that is emphasized by the transition state **TS_11**, located 102 kJ/mol above **P_99A** energy level. It is worth mentioning, that further separate ER-CID experiments performed on *m/z* 99 anion, required it's initial in-source generation. In this respect, we think that again here, the more thermodynamically stable isomer of m/z 99 anion **P_99A** is formed while generated in the ion source, from which further experimental measurements in the collision cell took place.

The DFT computations show that after transition state **TS_12**, the intermediate **P_99B** is formed, from which a exothermic path lead to the formation of anion *m/z* 41 by the loss of neutral molecule C_3H_6O. Fragmentation reaction mechanism has shown that anion *m/z* 41 refers to ketene anion structure. Notably, the experimental appearance energies for *m/z* 41 formation reaction estimated from experiments (72 (± 22) kJ/mol) and the computed energy values as an energy difference between **P_99A** and **P_41** (91 kJ/mol) show very good correlation. Respectively, anion *m/z* 55 is generated by decarboxylation reaction

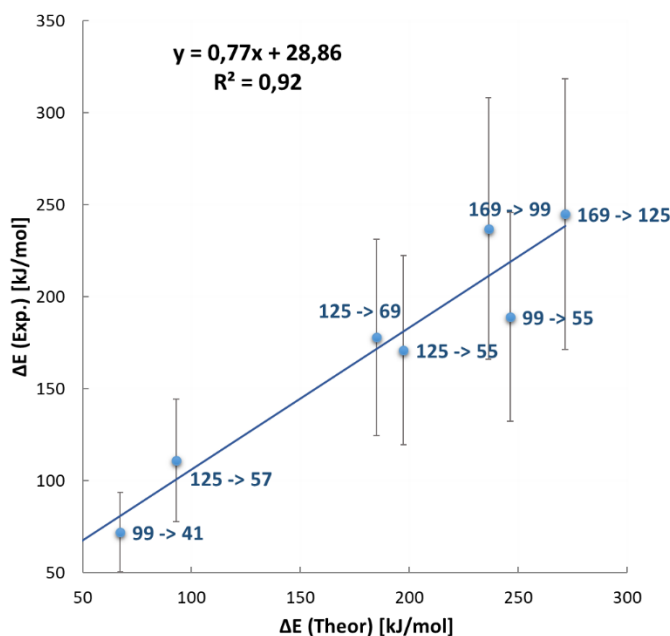
of anion m/z 99 (**IC_99**). The energy calculated for this process was found to be 252 kJ/mol. Calculated energy of anion *m/z* 55 formation reaction is slightly higher than experimental energy estimated with the extrapolation procedure which has been determined as 189 kJ/mol (Fig. 6, Table 1.).

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Figure 6. A correlation between experimental and theoretical fragmentation energies obtained with ωB97XD/6-311+G(2d,p) level of theory.

Table 1. Calculated electron energy values and experimental values in kJ/mol for fragmentation reaction of m/z 169 anion.

	Ion masses	Experimental Energy (kJ/mol)	Structure symbols	Theoretical method wB97XD/6-311+G(2d,p) (kJ/mol)
Fragmentation reaction	**169 → 99**	237 (± 71)	**S_169 → P_99A**	215
	99 → 55	189 (± 57)	**IC_99 → P_55**	252
	99 → 41	72 (± 22)	**P_99A→ P_41**	91
	169 → 125	245 (± 73)	**S_169→P_125A**	272
	125 → 69	178 (± 53)	**IC_125A→TS_5**	197
	125 → 57	111 (± 33)	**IC_125A→TS_8**	97
	125 → 55	171 (± 51)	**IC_125A→P_55**	257

230 The experimental and the theoretical insight into the fragmentation of deprotonated Norpinonic acid *m/z* 169 shown, that fragmentation through a four-member ring breaking, leading to *m/z* 99 is a more energetically favorable process than decarboxylation reaction. It was also reported than anion *m/z* 99 form two possible structures, which differ in the location of

the negative charge (**P_99A** and **P_99B**), see Fig. 4. Furthermore, from quantum chemical calculations, the existence of two possible structure were found also for anion *m/z* 69 (**P_69A** and **P_69B**) as well as, for anion *m/z* 125 (**P_125A** and **IC_125B**),

235   see Fig 4.

3.3 Proton Affinity analysis of anionic fragments

In order to provide more arguments and confirm ion structures formed during ER-CID experiments, we decided to examine the proton-transfer reactivity of all formed fragments towards few different proton-donors as neutral reagents, i.e. methyl thiocyanate (CH_3SCN), dimethyl disulfide (CH_3SSCH_3), chloroform ($CHCl_3$), bromoform ($CHBr_3$), dichloromethane

240   (CH_2Cl_2) and nitromethane (CH_3NO_2). The above chemicals have been chosen as a natural representation of species being present in the atmosphere, while their anions provides a wide range of Proton Affinity (PA) values that gives a chance to investigate a proton transfer reaction with Norpinonic acid fragmentation products (Van Den Berg, 1993; Van Den Berg et al., 1994; Watts, 2000; Khalil and Rasmussen, 1999; Jia et al., 2018; Hossaini et al., 2017; Graedel, 2012). The following Norpinonic acid anionic fragments were isolated as a result of the in-source generation/fragmentation and subjected into

245   collision cell to perform a bimolecular reaction w neutral species: $C_9H_{13}O_3^-$ (*m/z* 169), $C_8H_{13}O^-$ (*m/z* 125), $C_5H_7O_2^-$ (*m/z* 99), $C_3H_5O^-$ (*m/z* 57), $C_4H_5O^-$ (*m/z* 69), $C_4H_7^-$ (*m/z* 55) and C_2HO^- (*m/z* 41). Neutral reagents were introduced to the collision cell *via* an in-house built gas inlet system. For more details of the reaction conditions (vapor pressure of neutral reagents and E_{CM}), please consult the Supplementary Information. The reactions in the gas phase between neutral reagents and generated anions have shown a number of a new products, which will be described and published in other work in near future. In this publication,

250   the structural analysis of generated fragment anions will be performed based on the proton transfer reaction, which relies on differences between the proton affinities values of reacting ions and anionic forms of the vaporous neutral molecules. In Table 2 the results of the observed reactivity of fragment anions with a series of neutral reagents in proton transfer reaction is briefly summarized.

Table 2. Proton transfer reaction observed with gas-phase reactions of generated anions with series of neutral reagents (✓ - reaction
255   **observed, − - reaction not observed).**

A⁻	Proton transfer					
	CH_2Cl_2	$CHBr_3$	$CHCl_3$	CH_3NO_2	CH_3SCN	CH_3SSCH_3
m/z **169**	−	−	−	−	−	−
m/z **125**	−	✓	✓	✓	−	−
m/z **99**	−	✓	✓	✓	−	−
m/z **69**	✓	✓	✓	✓	✓	✓
m/z **57**	−	✓	✓	✓	−	−
m/z **55**	✓	✓	✓	✓	✓	✓

m/z **41**

Proton affinity for each possible fragmentat anion and for appropriate anions of the involved neutral reagents have been computed at ωB97XD/6-311+G(2d,p) level of theory are schematically presented in Fig. 7. For exact proton affinity values calculated at CAM-B3LYP/6-311+G(2d,p) and PBE1PBE/6-311+G(2d,p) level of theory please see Supplementary

260 Information. Proton affinities calculated for all fragment anions are within the range of 1378 kJ/mol for deprotonated Norpinonic acid (*m/z* 169) to 1709 kJ/mol for anion $C_4H_7^-$ (*m/z* 55). Computed structures of anion *m/z* 69 - **P_69A** and **P_69B** (see Fig. 4) have shown a significant difference in their proton affinity values. For anion **P_69A** proton affinity was calculated to be 1611 kJ/mol, while for structure **P_69B -** 1530 kJ/mol. The significant difference in proton affinity values was also found for two possible structures calculated for anion *m/z* 125. Proton affinity of structure **P_125A** was calculated at 1703 kJ/mol,

265 while for structure **IC_125A -** 1558 kJ/mol. Proton affinity analysis has shown that structure **P_125A** is stronger base than structure **IC_125A**. Similar dependence has been also reported for structure **P_69A** and **P_69B**, where structure **P_69A** is a stronger base than structure **P_69B.** The proton affinity values computed for appropriate anions derived from neutral reagents proton affinities were found to be from 1468 kJ/mol for bromoform anion to 1570 kJ/mol for dichloromethane anion. Computed PA values for deprotonated neutral reagents were consulted with experimental ones available in the literature and are in good

270 agreement (Afeefy et al., 2011).
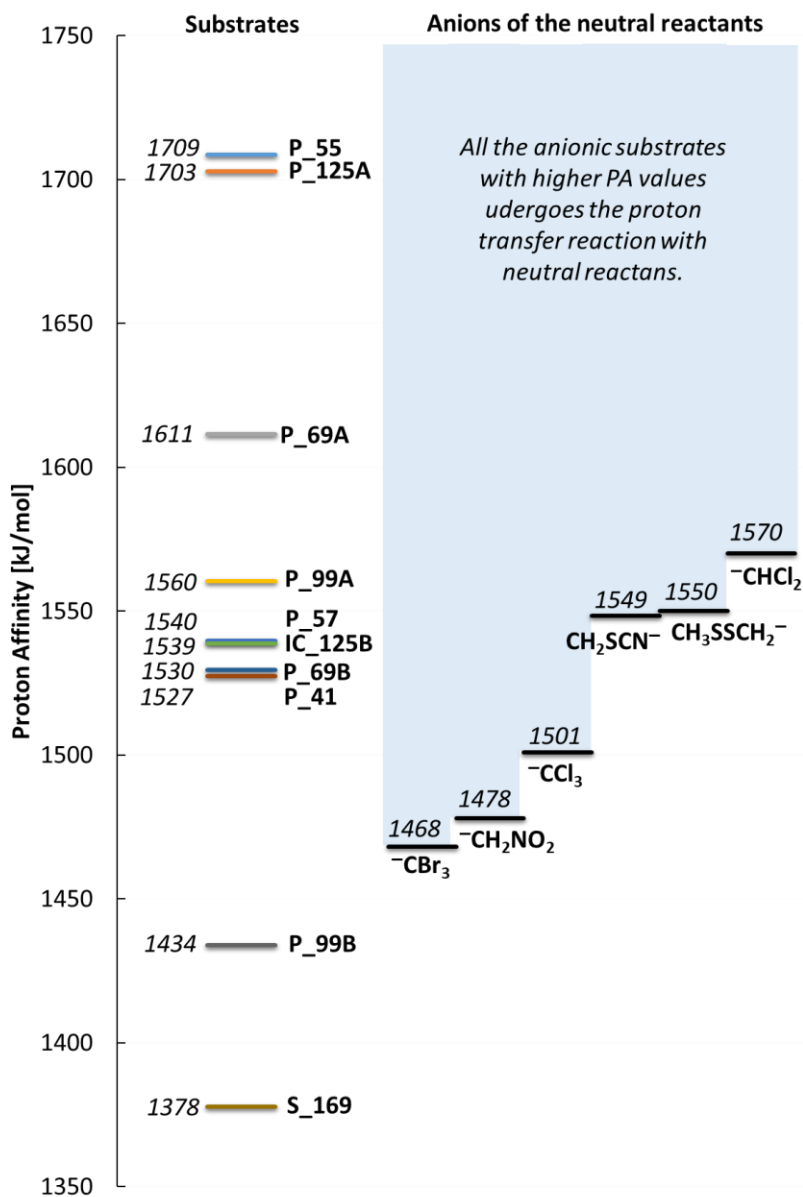
Figure 7. Proton affinity of the anionic fragment structures, compared with proton affinities of appropriate deprotonated reagents used in gas phase reactions obtained by theoretical calculation.

The proton transfer reaction with all neutral reagents was observed only for anions *m/z* 69 and *m/z* 55. Dichloromethane was found to react rapidly with anion *m/z* 55 in proton transfer reaction, the relative intensity was the most abundant since for anion *m/z* 69 reaction product appeared in a small amount. Similar results were obtained in reaction with methyl thiocyanate as well as, with dimethyl disulfide. The relative intensity of the products for both reagents was low − 2.0 % for anion *m/z* 55 and 0.1 % for anion *m/z* 69 (dimethyl disulfide reaction), 1.8 % for anion *m/z* 55 and 0.1 % for anion *m/z* 69 (methyl thiocyanate

reaction). In the reaction of generated fragments with chloroform, bromoform as well as nitromethane we obtained
similar/comparable results. The proton transfer reaction was observed for all studied fragments, except anion m/z 169. Anions
m/z 125, m/z 57 and m/z 55 were found to react rapidly with chloroform, the products of proton transfer reaction were the most
abundant. For reaction towards nitromethane, high intensity of proton transfer reaction product was observed for anions m/z
55 and m/z 57. Mass spectra of the reaction of chloroform, bromoform, dichloromethane and nitromethane towards anion
$C_9H_{13}O_3^-$ (m/z 169), $C_8H_{13}O^-$ (m/z 125), $C_5H_7O_2^-$ (m/z 99), $C_3H_5O^-$ (m/z 57), $C_4H_5O^-$ (m/z 69), $C_4H_7^-$ (m/z 55) and C_2HO^- (m/z
41) together with a relative intensity of proton transfer reaction product are presented in Fig. 8. For mass spectra of the reaction
with methyl thiocyanate as well as, with dimethyl disulfide please consult Supplementary Information.
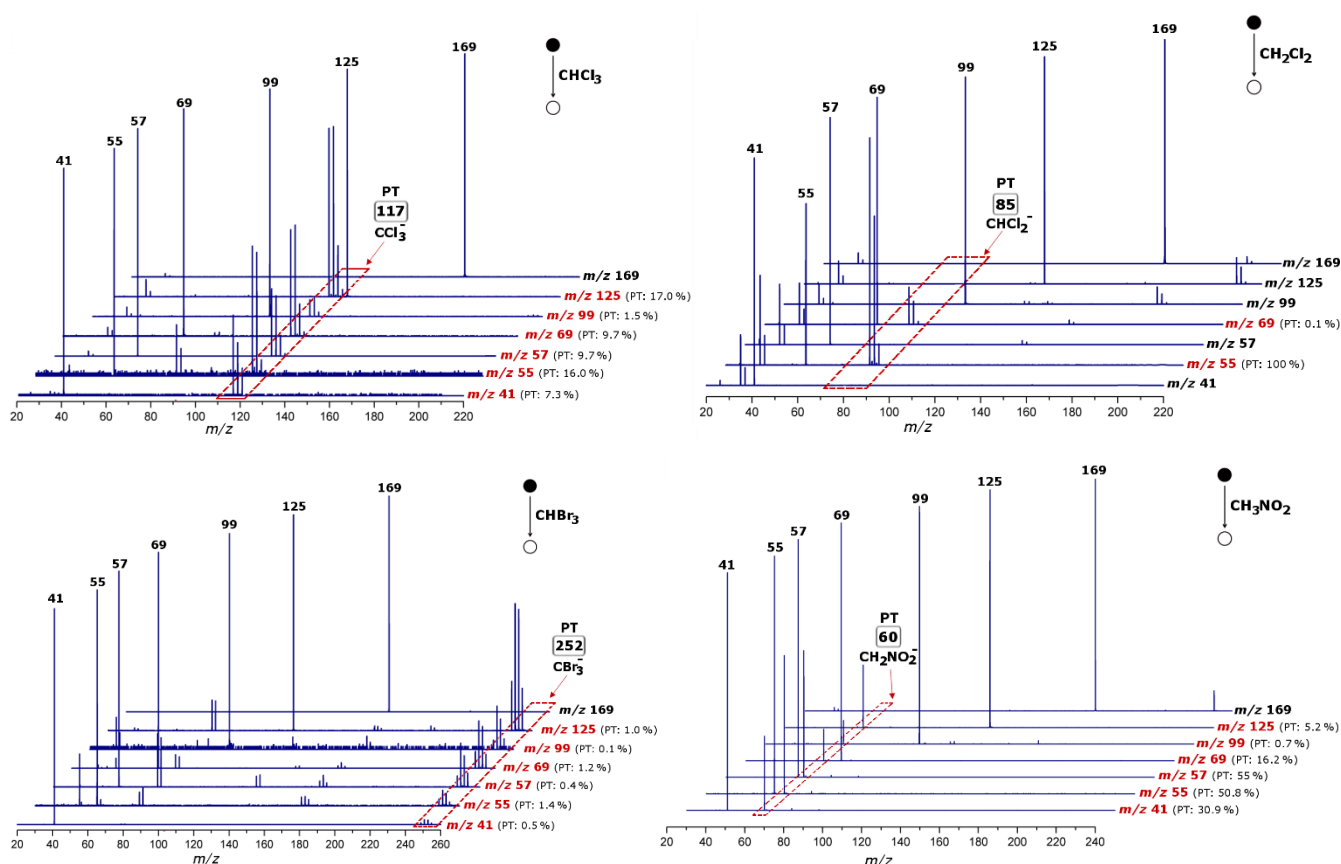
Figure 8. Mass spectra of the reaction between chloroform, bromoform, dichloromethane and nitromethane and generated in the ion source fragments recorded with a ToF voltage of 3kV, taken with reagents vapors at nominal pressures 3.25×10-4 mBar, 2.5×10-4 mBar, 3.05×10-4 mBar 3.14×10-4 mBar, respectively. For a collision energy for each anion (ECM) please consult the Supplementary Information.

Quantum chemical calculations and gas – phase reactions together with proton affinity analysis turned out to be important to
distinguished the structures formed during the collision-induced dissociation (CID) experiments. Quantum chemical

calculations have shown two possible structures of anion *m/z* 125. However, an analysis of secondary fragmentation products of anion *m/z* 125 together with analysis of threshold energies, have shown that **P_125A** is able to rearrange to the more stable structure **IC_125A**. It appears rational that anion **P_125A** is formed in the collision cell during CID experiments of the precursor ion *m/z* 169 – experimental and theoretical threshold energies shown good correlation, while in the ion source,

300 generated anion can rearrange to the more stable linear structure **IC_125A**. Furthermore, in the gas-phase reaction between anion *m/z* 125 and dichloromethane, methyl thiocyanate as well as, dimethyl disulfide proton transfer reaction products were not observed. This argument also confirms the hypothesis of the two possible structure of anion *m/z* 125, since proton affinity value for **P_125A** was calculated to be 1703 kJ/mol (proton transfer reaction product expected), since for structure **IC_125A** 1558 kJ/mol (value lower that proton affinity of dichloromethane, methyl thiocyanate and dimethyl disulfide – a proton transfer

305 reaction should not occur and was not observed). Two possible structures have been also computed for anion *m/z* 69. It was found that anion **P_69B** need slightly lower energetic requirements to be formed, than anion **P_69A**, but the difference is not significant to unambiguously indicate the structure **P_69B** as the one. For anion *m/z* 69 a small amount of product of proton transfer reaction was observed in reaction with all neutral reagents, which clearly proves the presence of **P_69A** during ER-CID experiments. However, the combination of the lower energetic requirements obtained from quantum chemical

310 computation for anion **P_69B** together with a higher proton affinity for **P_69A** has shown that both structures are possible to be generated in ER-CID experiments. In accordance with the computational model anion *m/z* 99 can form two possible structures, a first, where anion is located on the carbon atom (**P_99A**) or second, where anion is localized on oxygen atom (**P_99B**). Calculated PA value for structure **P_99A** is 1557 kJ/mol, while for **P_99B** 1449 kJ/mol. The gas-phase reactions of the *m/z* 99 anion with chloroform, bromoform and nitromethane give rise to a detectable amount of proton transfer reaction

315 products, which clearly indicates the presence of at least some of **P_99A** structures during ER-CID experiments.

4 Conclusion

The study of the fragmentation pathways of deprotonated Norpinonic acid (important α-pinene oxidation product) was conducted together with structural analysis of the fragments generated during the energy resolved collision-induced dissociation (ER-CID) experiments. We have shown that quantum chemical calculations and gas-phase reactions supported

320 by proton affinity analysis are reliable methods for the structural analysis of the deprotonated Norpinonic acid (*m/z* 169) fragments. We have conducted a number of ER-CID experiments with a modified Q-TOF type mass spectrometer. Subjecting the anion *m/z* 169 to collisional activation leads to the formation of fragment ions corresponding to $C_8H_{13}O^-$ (*m/z* 125), $C_5H_7O_2^-$ (*m/z* 99), $C_3H_5O^-$ (*m/z* 57), $C_4H_5O^-$ (*m/z* 69), $C_4H_7^-$ (*m/z* 55) and C_2HO^- (*m/z* 41) anions. The breakdown curves for all fragment ions were also measured at variable collision energies and at five different collision gas pressures to estimate the threshold

325 energies, which were measured to be from 72 kJ/mol for *m/z* 41 formation reaction to 245 kJ/mol for ion *m/z* 99 formation. Further insight into the observed fragmentation pathway of deprotonated Norpinonic acid was obtained through quantum chemical calculations. Reaction models for observed fragmentation processes were constructed, including calculation of all

transition states presented in the reaction mechanism. Comparison between the experimental and the theoretical threshold energies calculated with ωB97XD/6-311+G(2d,p) level of theory has shown a very good correlation - coefficient of
330   determination (R^2) was found to be 0.92.

Finally, to distinguished all possible ion structures generated during ER-CID experiments, we examined the reactivity of all fragments towards a series of different neutral reagents - methyl thiocyanate (CH_3SCN), dimethyl disulfide (CH_3SSCH_3), chloroform ($CHCl_3$), bromoform ($CHBr_3$), dichloromethane (CH_2Cl_2) and nitromethane (CH_3NO_2). Neutral reagents were introduced to the collision cell *via* an in-house built gas inlet system. For structural analysis of generated anions, products of
335   the gas - phase reactions were analyzed for proton transfer reaction. The possible structures were proposed for all observed during ER-CID experiments anions, it was also found that anions *m/z* 125, *m/z* 99 and *m/z* 69 can formed two possible structures.

Quantum chemical calculations and the gas-phase reactions together with proton affinity analysis turned out to be an valuable method to reflect the proper structures formed during energy-resolved collision-induced dissociation (ER-CID) experiments.
340   Fragmentation structure proposed for an important α-pinene aging product (Norpinonic acid), serve as a useful databank for the atmospheric community and is believed to be extended in the future, towards other important aerosol products, including different monoterpene SOA.

Author Contributions

IK performed a part of DFT computations and co-write the manuscript, AB performed the experiments and DFT computations,
345   KP analyzed a part of experimental breakdown curves, KK co-write the manuscript, co-write the manuscript, KB coordinated the project, experiments and theoretical computations, co-write the manuscript. All authors have given approval to the final version of the manuscript.

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350   **Competing interests**

The authors declare no competing financial interest.

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500