

Reviewer1

Minor comments:

Page 1, line 8. According to EGU standards, abbreviations need to be defined at the first instance of use. Here, it should be "Secondary Organic Aerosol (SOA)". Please also check other abbreviations, e.g. in the abstract, "CIE" was used the same way as SOA, and "ER-CID" was used without a definition.

Corrected.

Page 1, line 10. "O₃" with subscript.

Corrected.

Page 1, line 29. "Primary organic aerosols" are emitted directly into the atmosphere.

Corrected.

Page 2, line 40. "a few"?

Corrected.

Page 2, line 56. Since "O₃" has already been defined, it can be used directly here. Please also check other abbreviations used in this manuscript.

Corrected.

Page 2, line 58. "0.2 – 1.1 ng·m⁻³" is not significant compared to the total organic mass (e.g. <5 μg m⁻³ in clean areas or ~15 μg m⁻³ in the paper you referred). In either case, norpinonic acid contributes less than 0.1%. You may want to mention that mono-/di- carboxylic acids are identified in SOA in large amounts, and norpinonic acid (containing one carbonyl and one carboxylic acid functional group) is chosen as an example to investigate how organic acids fragment to rationalize why you focused on this specific compound.

Corrected.

Page 3, line 79. Can you provide/estimate the purity of the synthesized cis-norpinonic acid used in this study? In addition, do you think that there would be any potential by-products or contamination during the synthesis process that might affect the analysis in this study?

The purity of the synthesized products was not demined in details and not quantified. The synthetic clarity and identity was made based on NMR spectra and no percentage purity value was defined. However, the analysis of NMR qualitative spectra (the SI chapter 1.2) of the synthetic acid was positive and high-resolution mass spectra confirmed the proper atomic composition of recorded mass peaks. On the other hand, the presented mass spectrometry studies are not very sensitive to the potential impurities, because while the mass signals are quadrupole-selected other ions are eliminated from ion beam and do not interfere with the target molecules.

Page 4, Section 2.3. Can you explain in detail how you deal with conformers, e.g., the criteria for potential duplicates based on electronic energy or electric dipole, so that others may reproduce the calculations if they want?

Statistical analysis using Boltzmann equation and resulting state distribution was used to select the most abundant conformer among others. The computed Gibbs free energies were taken into analysis and percentage distribution for all conformers was made, based

on which the most stable one was selected for further computational consideration. - Appropriate comment was added into the text of the publication.

Page 4, subtitle 3.1. Fragmentation pathway of “Norpinonic acid anion”.

Corrected.

Page 5, line 127. Is Supplementary Information (SI) Section 2 related to this discussion? Please specify which section and/or figure you refer to in the manuscript, as it's hard for readers to find relevant parts within the 59-page supplementary material. Try to avoid simply stating "Please consult the SI". Check other parts in the manuscript (e.g., lines 161, 248, 256...) that refer to supplementary material without specifying which part(s).

Appropriate references have been made.

Figure S3, “m/z 57” should be “m/z 41”.

Corrected.

Figure 3. Can you add which neutral part has been lost along with the arrows? For example, the arrow from m/z 169 to m/z 125 represents the loss of CO₂. This clarification may help non-chemist readers follow the process more easily.

Corrected.

Page 7, lines 141 and 142. Are “237” and “245” correct? Or should they be swapped? In line 179, you used “245” for the pathway that forms m125, while in line 211, you also used “245” for the pathway that forms m99. It is very confusing. Also, in line 153, the onset energies “171” seem to contradict the values in Figure 3 (there was no “171” in Figure 3). Please double-check all these values in the figures, tables, and corresponding discussions.

Corrected.

Page 7, line 152. Please change “followed by” to “along with”.

Corrected.

Page 7, line 160. Why do you think “the ω B97XD hybrid density functional method reproduces the experimental observation the most accurately” than other methods?

The computational method that most closely matched the experimental results was chosen on the basis of the correlation coefficients between experimental and computed results. The correlation coefficient for the ω B97XD method was $R^2 = 0.92$ (Fig. 6), while the ones for the other two was 0.85 and 0.83 (PBE1PBE and B3LYP, respectively, Fig. S62, S63). - Appropriate comment was added into the text of the publication.

Page 8, line 173. Is “58” correct?

Corrected.

Page 10, line 212. Should “P_99B” be “IC_99”?

Corrected - There should be three fragmentation products, information about additional intermediate product was added.

Page 13, line 257. “fragmentat”?

Corrected.

Reviewer2

Minor comments:

1) Norpinonic acid is a semi-volatile product which resides in both gas and particle phase. These fragmentation patterns refer to gas phase. How much important is its gas phase with respect to the particle phase? Do you have an estimation of how much volatile it is? (any measurements or estimations from the literature). This research becomes more valuable if you show that the gas phase is important (i.e., norpinonic acid resides in the SVOC regime). This discussion should be added in the Introduction.

(Shao et al., 2022) Norpinonic acid is considered a semi-volatile organic compound (SVOC) with a vapor pressure of about 1.28×10^{-4} Torr,[cytownie] making it a slightly more significant contributor to the gas-phase air chemical composition than pinic, pinonic, or norpinic acids. Considering this, the potential gas-particle phase transition of Norpinonic acid suggests that it's kinetic transformations in gas phase may play an important role in atmosphere evolution.

2) Are there any previous literature describing the fragmentation pattern of other important α -pinene SOA products? (e.g., pinic acid, pinonic acid, norpinic acid, etc.?). If yes, how much similar, or different is their fragmentation? How, much easy or difficult would be to distinguish norpinonic acid from other α -pinene SOA products in an ambient sample?

To our best knowledge there is no literature examples in which the energy-resolved fragmentation patterns have been recorded for other atmospheric relevant compounds. There is no information about the energetics of fragmentation or bond breaking process for other acids. The MS/MS mass spectra can be only compared while registered in the same conditions (collision gas pressure and kinetic energy). We are aware, that mass spectrometry has been widely used in analytical atmospheric chemistry and fragmentation spectra has been recorded for various of other air-present acids. This suggestion is very valuable, but we do not plan to expand current paper by this data because it requires a detailed analysis and will make it unacceptable long. In parallel, we are currently working on a very similar project where series of acids and their fragmentation patterns, together with detailed energetics will be compared by using highly advanced statistical methods.

Technical corrections:

Page 1, Line 10: Please replace "O3" with "O₃".

Corrected.

Page 1, Line 31: "from a biomass burning" delete "a".

Corrected.

Page 2, Line 34: Please replace "result with" with "result in".

Corrected.

Page 2, Line 37: Please replace "among which, compounds with carboxylic functional groups are observed in large amount." with "among which, a large number of compounds containing carboxylic functional groups".

Corrected.

Page 2, Line 42: Pathak et al., 2007 is a chamber study, without chemical analysis, so, it doesn't fit here.

Deleted.

Page 2, Line 44: Please add more recent studies.

Reference were added.

Page 2, Line 54: Please replace "during the field or ambient samples analytical process" with "during ambient samples analytical process".

Corrected.

Page 3, Line 69: "to initiate of each" please delete of.

Corrected.

Page 3, Lines 74-76: Expanding.... atmosphere" Please rephrase the sentence.

Rephrase.

Page 3, Line 80: Please replace "method by Moglioni et al. (Moglioni et al., 2000)" with method by Moglioni et al. (2000)".

This way of writing is due to the journal's guidelines on how to cite.

Page 3, Line 96: Please replace "In presented studies" with "in the present study".

Corrected.

Page 4, Line 119 and Page 5, Figure Caption 1: Please replace " 3.54×10^{-4} " with " 3.54×10^{-4} " (in several places in the manuscript " 10^{-4} " should be replaced by " 10^{-4} ").

If I understand correctly, the idea was to use a high index. Corrected.

Page 7, Line 148: Please replace "the m/z 69 anion" with "m/z 69 anion".

Corrected.

Page 7, Line 149: Please replace "Second pathway," with "The second pathway,".

Corrected.

Page 7, Line 161: Please replace "comparison the other" with "comparison with the other".

Corrected.

Page 8, Line 171: "Rearrange" with "be rearranged".

Corrected.

Page 8, Line 174: Please replace "by Yasmeeen, F. et al.," with "by Yasmeeen et al. (2010)".

This way of writing is due to the journal's guidelines on how to cite.

Page 8, Line 176: "understanding of the" please delete "of".

Corrected.

Page 8, Lines 176-178: While....is formed" The syntax of this sentence doesn't seem correct, please rephrase it.

Corrected.

Page 8, Line 179: Please replace “fact the excellent” with “fact an excellent”.

Corrected.

Reviewer3

General comments:

1) Please improve the structure of the abstract. Abstracts should have fewer than 250 words. Also, authors focus more on the approach and results/observations, but it is not clear to me about the status of research, research gap, the importance and implications of the results.

Abstract was improved.

2) In this study, you studied the Norpinonic acid anionic fragmentation pathway in the gas phase. But in the Introduction section, you mentioned more analytical techniques that used for OA products (Lines 44-47). This might be confusing. I suggest that you should focus more on the gaseous measurements.

Both aspects are important, and because the analytical techniques are the most popular tools in which the fragmentation technique is used to identify SOA molecules we decided to focus more on this matter in the introduction giving just a signal that the degradation/fragmentation process is of interest in gaseous environment. As the Reviewer suggested the gas-phase measurements are the other side of moon, as much important but there is a lack of direct chamber or field experiments that we could refer to in the case of fragmentation SOA phenomena. Taking above we opt to address this results mainly to the analytic chemists giving them a deep insight on how the structure identification of fragment ions can be accompanied by reaction energy analysis.

3) Lines 52-53: "to the proper identification of OA components, mentioned MS/MS measurements should be made very accurately", I suggest that you could add more descriptions/discussions about the MS/MS technique here.

The appropriate references to MS/MS type of analytical technique has been added to the text, giving access to more detailed method descriptions elsewhere.

4) Line 156: why do you apply three different DFT methods in this study?

We added this information to SI section 4. Computed data for norpinonic acid:

Because density functional methods are best regarded as approximations to the resolving for the electron density in a molecular system and the exact exchange correlation function is not known, comparative analysis of different DFT models in terms of performance is an important part of computational chemistry. Quite often, one particular set of functionals and functional bases works very well for a particular application, so for the study of structures not precisely described by quantum chemistry, calculations should be carried out with various functionals to get closer to experimental results.

5) Lines 160-161: For the comparison, please state the specific difference or improvement between these three methods here.

The computational method that most closely matched the experimental results was chosen on the basis of the correlation plots of the results. The correlation coefficient for the ω B97XD method was $R^2 = 0.76$ (Fig. 6) while that for the other two was 0.75 and 0.53 (PBE1PBE and B3LYP, respectively, Fig. S63, S64).

6) Section 3.1: Is this the first research that emphasize fragmentation pathways of norpinonic acid? Are there any other comparable studies, please add more discussion in this Section.

To our best knowledge there is no literature examples in which the energy-resolved fragmentation patterns have been recorded for other atmospheric relevant compounds. There is no information about the energetics of fragmentation or bond breaking process for other acids. The MS/MS mass spectra can be only compared while registered in the same conditions (collision gas pressure and kinetic energy). We are aware, that mass spectrometry has been widely used in analytical atmospheric chemistry and fragmentation spectra has been recorded for various of other air-present acids. This suggestion is very valuable, but we do not plan to expand current paper by this data because it requires a detailed analysis and will make it unacceptable long. In parallel, we are currently working on a very similar project where series of acids and their fragmentation patterns, together with detailed energetics will be compared by using highly advanced statistical methods.

7) Lines 129, 161, 248, 286, 292: *It is hard for readers to connect the main text with the SI, here you do not provide the relevant parts in the SI.*

Appropriate references have been made.

8) Line 29: *should be: "Primary organic aerosols are emitted to the atmosphere..."*

Corrected.

Technical corrections:

Line 8: *"athmospheric"*.

Corrected.

Line 11: *please provide the full title of m/z.*

The appropriate reference to the definition of m/z abbreviation has been added. The IUPAC description of mass to charge ration, should help the readers to understand the proper meaning as unified and commonly acceptable description.

Link: <https://goldbook.iupac.org/terms/view/M03752>

Line 13: *Is "CIE" right?*

Corrected. It should be Energy-Resolved Collision Induced Dissociation (ER-CID) technique.

Line 21: *please provide the full title of ER-CID when it occurs at the first time*

Corrected.

Line 119, Line 128: *superscript: "10⁻⁴".*

Corrected.

Line 257: *"fragmentat"*

Corrected.

Reviewer4

General comments:

This manuscript takes many contents to discuss results from computed potential energy and reaction energy. However, there is no any information to explain this in the introduction and method.

In gas-phase mass spectrometry experiments, the reaction energy in the form of kinetic energy required to cleave interatomic bonds is measured during CID (Collision-Induced Dissociation) experiments by effective collisions with neutral Argon gas. The potential energy surface, or the potential energy, is represented by the computationally predicted reaction mechanism with transitional and stationary molecular energy levels. The reaction/kinetic energy is measured dynamically by the mass spectrometry experiment, while the potential energy is proposed by the model. However, both are comparable since they describe the same phenomenon and the same molecular transformations.

Special comments:

Line 50-55. It needs to give more information about MS/MS techniques.

Citation added.

Line 129, 292. When you mention the supplementary information. Please explain where the information comes from. It is hard to find out where it is.

Appropriate references have been made.

Line 156-157. It should use some references to explain the different DFT methods and give more information about those methods.

More information about Gaussian 09 program were added in SI, section 4. Computed data for norpinonic acid.

Figure 7. This figure gives a little information. However, this figure is too big. It is better to make it more sample and useful.

The figure has been moved to the SI, and a smaller and more readable table has been placed in the article.

Reviewer5

How should we link the experimental results to the current atmospheric chemistry? Will the fragmentation of norpinonic acid in the gas phase have much effect on the natural atmospheric aerosol formation?

Since, there is no current knowledge on detailed mechanisms of gas-phase fragmentation/degradation process in atmosphere. Only some chamber experiments show the decline of SOA in the function of time, we decided to give a first experimental and theoretical insight into possible fragmentation/degradation scenario. It is difficult to predict whether natural atmospheric aerosol fragmentation proceeds directly via presented energy regime since there are no field experiments that would try to follow that. The presented results should be considered as a model reaction, measured and computed in the laboratory environment serving as a first example, pointing out that this process is observable.

Other comments:

1. *It is not proper to use the abbreviation "DFT" in the title directly. Also, I haven't seen any explanation about "DFT" in the main text.*

I respectfully disagree. In publications containing quantum chemistry results, this is an abbreviation commonly used, immediately indicating the method used for quantum chemical calculations.

An expanded abbreviation in the description of the methodology has been added.

2. *Line 80: More details should be described in the main text, i.e., what is the main mechanism used for the synthesis of cis-norpinonic acid, what is the purity of the synthesized product? Why the trans-norpinonic acid is not used here?*

Information about the synthesis process is not the main topic of the publication, the decision was made to fully explain the methodology, together with NMR spectra, in the SI. It also mentions that NMR measurements showed the presence of the cis stereoisomer of norpinonic acid. Therefore, this exact stereoisomer was used for the quantum chemical calculations.

The main text mentions that details are included in the SI: *A detailed synthetic procedure for the preparation and purification of the norpinonic acid along with the IR, ESI-HR-MS, 1H and 13C NMR analytical spectra of the final product are provided in Supporting Information.*

3. *Lines 105-106: The description of the calculation is quite simple, could you add some more details about the Gaussian 09 suite of programs and the Cartesian coordinates of the initial geometries here?*

More informations about Gaussian 09 program were added in SI, section 4. Computed data for norpinonic acid.

The Cartesian coordinates of all optimised structures are shown in the SI. The initial structure of norpinonic acid was generated using data from <https://pubchem.ncbi.nlm.nih.gov/compound/129690414> (accessed: 20.05.2024). The other structures were determined based on transformation calculations from subsequent fragmentations.

4. *Line 223-225: the variations in the averaged experimental fragmentation energies are quite large (with large averaged standard deviation), how will these uncertainties affect the results and discussions in Sect. 3.2?*

We are aware of the presented uncertainties can be considered as a large by numbers. Since, there is no "golden" standard which could be used to validate the energetic measurements, the commonly accepted strategy to calculate the experimental error is to summarize the uncertainties each measuring device, such as: pressure gauge, energy distribution within the ion, R2 deviation form ideal linear fit. All of this gives more less 20-35% cumulative possible error and this is presented to give the honest possible area of uncertainty which may occur formally. However, the measured experimental values in most of the cases do match the computationally predicted energy counterparts correctly in absolute manner and we do not expect based on our experience that the error exceed 15-20%.

5. *Lines 227 and 255: please keep the table format the same.*

Corrected.

6. *In the conclusion section, please summarise more on the experimental results and their significance rather than the experimental method and procedures.*

Corrected.

Reviewer6

1. In introduction Line 63, the authors mentioned about the breakdown process of SOA into fragments within ionic chemical transformation. However, this study focuses on Norpinonic acid (an α -pinene derived SOA component) anionic fragmentation pathway in the gas phase. If I understand correctly, the fragment ions can be used as a fingerprint to characterize Norpinonic acid in SOA samples using tandem mass spectrometric analysis. If so, can this be mentioned as a SOA composition characterization technique in the Introduction part to better connect the importance (i.e., atmospheric relevance) of the work? Besides, do the authors expect any similarity or differences between the fragmentation patterns of Norpinonic acid and the other α -pinene derived acids (or isomers) so that they can be distinguished from each other?

This issue is a matter of our second ongoing project where different fragmentation patterns, their energetics and possible product structures will be compared and statistically analyzed. And since current paper is the very first gas-phase analysis of energy dependences in SOA fragmentation pattern we decided to focus only on one SOA acid.

2. In the quantum chemical calculation section, the authors used three methods for comparison. I would expect to see some kind of calculation strategy (e.g., as a flow diagram or a detailed text) starting from conformer sampling to global minima geometry optimization step if it is done in that way. In other words, explaining the stepwise procedure adopted in the calculations will be appreciated. The authors might want to check Fig.1 of the reference below: Seal et al., *A systematic study on the kinetics of H- shift reactions in pristine acyl peroxy radicals*, *Phys. Chem. Chem. Phys.*, 2023, 25, 28205–28212.

Thank you for this interesting idea. Appropriate shame was added to SI.

3. In this work, the structural analysis of the fragment ions is done based on their relative proton affinity (PA) values. The percentage of proton transfer reaction between the fragment anions and a particular neutral reagent is consistent with their PA differences (Fig. 8). In the case of bromoform (CHBr_3) as neutral reagent, the PA difference between its anionic form (CBr_3^-) and the fragment anions is the highest compared to other reagent anions (e.g., CCl_3^- , and CH_2NO_2^-). However, percentage of proton transfer reaction with CHBr_3 is less than that of CCl_3 and CH_3NO_3 . Is this somehow possible to the reason behind the observation?

The proton-transfer experiment has only qualitative character. It is not possible directly to link the intensity of the product ion with the amount of product since we are unable to track the energetics in this part of the bimolecular measurements, which means that we can only observe if the proton-transfer occur or not and can distinguish them by energy.

Other comments:

4. In abstract Line 10, use subscript for “ozone (O_3)” instead of “ O_3 ”. Also, “In the present study, tandem ...” instead of “In the presented studies”.

Corrected.

5. In Line 13, “energy-resolved collision induced dissociation (ER-CID)” instead of “CIE (Energy-Resolved Collision Induced Dissociation)”

Corrected.

6. In Line 19, Please consider rephrasing and correcting as “Loss of $\text{C}_3\text{H}_6\text{O}$ and CO_2 molecules together with the formation of anions m/z 41 and m/z 55 were found for the fragment anion m/z 99.” instead of “Loss of C_3H_6 or $\text{C}_2\text{H}_4\text{O}$ ”

Corrected.

7. In Line 20, “ On the other hand, the break down of anion m/z 125 gives a rise of m/z 69, 57, and 55 ions.” instead of “ Further breaks down ...”

Corrected.

8. In introduction Line 29, write “ Volatile organic compounds (VOC) ...” instead of “ Organic aerosols..” If the authors want to say aerosols/particles here, it is primary particles that directly emitted to the atmosphere.

Corrected.

9. On page 2 Line 33, it is not necessary to put the “ dot ” with OH and NO₃ radicals.

Corrected.

10. In Line 34, “result in the secondary organic aerosol (SOA) formation” instead of “ result with ...”

Corrected.

11. In Line 48, “ to identify and quantify the atmospheric aerosol polar and organic compounds.” instead of “ to identificate and the quantificate the ...”

Corrected.

12. In Line 52, “ However, to do the proper...” instead of “ However, to the proper”

Corrected.

13. In Line 57, consider writing as “Norpinonic acid is considerably significant which is about 0.2-1.1 ng.m⁻³”

Corrected.

14. In Line 63, starting with the transition signal “While” makes the sentence feel like incomplete. Try to use another signpost instead of “ while”.

Corrected.

15. On page 3 Line 70, please consider rephrasing the sentence or rewrite as “ the bimolecular reactions of Norpinonic acid anion and it s anionic fragments with a series of”

Corrected.

16. In Line 73, it is better to replace the word “ analyze” with something like “ study” to avoid the repetition of the word “ analysis” which is used in the beginning of the sentence.

Corrected.

17. In Line 82, please also mention the specific section of the Supporting Information, e.g., Supporting Information section 1.

Corrected.

18. In Line 90, just write “ For the ER-CID experiments, argon (Ar) was used as collision gas while ...”

Corrected.

19. In Line 96, “ In the present study” instead of “ In presented studies...”

Corrected.

20. On page 4 Line 98, how about “recording time” instead of “collection time”?

Corrected.

21. In Line 99, put a “comma” after the word “process”

Corrected.

22. In Line 118, use parenthesis for ECM “center-of-mass collision energy (ECM)”

Corrected.

23. In Line 119, use superscripts with the pressure values here and everywhere in the latter sections of the manuscript, e.g., “ 3.54×10^{-4} mbar”

Corrected.

24. On page 5 Line 127, specify the Supporting Information (SI) section here and everywhere in the manuscript.

Corrected.

25. On page 6 Figure 3, please check the numbers 237 kJ/mol and 245 kJ/mole with the gray arrows. They are likely interchanged and are inconsistent with the text. Also, check the structural formula of m/z 41 ($\text{H}-\text{C}=\text{C}=\text{O}$)–. It is missing one carbon atom with a C=C double bond.

The numbers and structure were corrected.

26. In Figure 3 caption, rewrite as “Please note that above (or below) the gray arrows” or “Please note that with the gray arrows”

Because of the captions above and below the arrows, we believe this description is more accurate.

27. On page 7 Line 144, use a “comma” after “ m/z 99”

Corrected.

28. In Line 145, refer to Fig. 5 here as “.... loss of the neutral molecule $\text{C}_3\text{H}_6\text{O}$ (see Fig. 5 below),”

Corrected.

29. In Line 146, refer to Fig. 5 here as “.... loss carbon dioxide molecule (see Fig. 5 below),”

Corrected.

30. In Line 147, remove “comma” after the word “shown”

Corrected.

31. In Line 149, refer to Fig. 4 here as “.... loss of the neutral molecule C_4H_8 (m/z 56) (see Fig. 4 below),”

Corrected.

32. In Line 150, refer to Fig. 4 here as “.... loss of the neutral molecule C_5H_8 (m/z 68) (see Fig. 4 below),”

Corrected.

33. In Line 152, replace “ followed by” with “by the splitting of the neutral molecule” or “ with the formation of the neutral molecule”

Corrected.

34. In section 3.2 Structural analysis of observed ion fragments, I strongly suggest to consider switching the numbers of Fig. 4 and Fig. 5 and the associated discussion. Bring the m/z 99 part first and then the m/z 125 part to keep the order consistent throughout the manuscript.

We opt to start the discussion with higher mass ions (m/z 125) and then continue with the smaller fragments (99) to make the journey more consistent and easier to follow while tracking the fragmentation pathway which starts with higher masses and ends with the small ones.

35. On page 8 Figure 4, in the potential energy diagram, label the neutral molecules with their molecular composition also, e.g., C_4H_6O (m/z 70), C_4H_8 (m/z 56), and C_5H_8 (m/z 68) for better readability. Same goes for the neutral molecules in Fig. 5.

We added the information about neutral molecules structure on the Figure 3. We think that now everything is clear. Adding this information to the theoretical energy diagram would negatively affect its readability.

36. In Line 173, isn't it that the TS_1 barrier is 51 kJ/ mole as per the figure labels (323-272) kJ/ mol?

Corrected.

37. In Lines 181 and 184, replace the words “ consequent” and “ sequent” by “ subsequent ” ?

Corrected.

38. On page 9 Line 185, remove “comma” after the word “shown”

Corrected.

39. In Line 197, authors mentioned about two different m/z 57 anion isomers. Indeed, I do not see two m/z 57 anion isomers in Fig. 4. Instead, I see that the barrier energy of 197 kJ/ mol for TS_4 is associated with the IC_{125A} to IC_{125B} conversion. Please, correct the text accordingly.

Corrected.

40. In Line 199, isn't it 97 (201-104) kJ/ mol as per Fig. 4 labels instead of 85 kJ/ mol?

Corrected.

41. On page 10 Figure 5, in the potential energy diagram, the anion P_{99B} is missing one carbon in its structural formula. The present formula shows that it is a C_4 system instead of what it should be a C_5 system. Please check also for the m/z 41 anion which is mentioned in an earlier comment.

Corrected.

42. In Figure 5 caption, write with more details as “ ... fragmentation pathway of m/z 169 ion via m/z 99.”

Corrected.

43. In Line 208, write “ in exothermic process” instead of “ on exothermically way”

Corrected.

44. In Lines 213 and 217, I think the authors are mixing up TS_11 and TS_12.

Corrected.

45. In Line 213, isn't it should be written as “transition state TS_12, located 70 (286-216) kJ/ mol above P_99A energy level.” when the authors are describing the isomer P_99B?

Corrected.

46. In Line 217, replace the word “ intermediate” with “ isomer ” before P_99B.

Corrected.

47. In Line 221, remove the word “ Respectively”, instead write as “ The anion m/z 55 is”

Corrected.

48. On page 11 Figure 6, please double check the X-axis and Y-axis labels and the position of data points, e.g., theoretical value for 125 → 55 is 257 (in Table 1) is not consistent with Fig. 6. Same goes for other data points.

Figures were corrected.

49. In Table 1, please double check the theoretical values if they are consistent with the numbers in Fig. 4 and Fig. 5, e.g., shouldn't it be 216 (S_169 → P_99A) instead of 215, and 200 (IC_125A → TS_5; 304-104) instead of 197?

Corrected.

50. In Line 230, “ show that ” instead of “ shown, that ”

Corrected.

51. In Line 234, for anion m/z 125, the authors mentioned about the structures of P_125A and IC_125B. How about IC_125A and IC_125C?

Corrected. We changed IC_125B to P_125B.

52. In Line 245, “ reaction with neutral species ...”

Corrected.

53. On page 13 Line 265, there is a discussion is about IC_125A. However, in Fig. 7, IC_125B is included instead of IC_125A. Is there any reason for that?

We change IC_125A to IC_125B.

54. In Line 269, replace the word “ consulted” by “ compared”

Corrected.

55. On page 14 Lines 275-276, consider rephrasing the sentence if possible.

Corrected.

56. On page 14 Line 276, refer to Fig. 8 here as “ in a small amount (see Fig. 8).”

Added.

57. On page 14 Line 277, it will be nice to have the figures for thiocyanate and dimethyl disulfide in the SI and link them here.

The figures (chemical structures) of thiocyanate and dimethyl disulfide in their anionic form has been presented in the SI next to the cartesian coordinates.

58. On page 15 Line 281, why not m/z 69 also included here since it reacts as rapidly as m/z 57 (both with PT: 9.7%)?

Corrected.

59. Line 283, Is there any reason why the percentage of proton transfer for m/z 55 (PT: 50.8%) is less than that of m/z 57 (PT: 55%) in Fig. 8 although proton affinity difference between P_{55} and $CH_2NO_2^-$ is higher than the difference between P_{57} and $CH_2NO_2^-$ in Fig. 7? Can it be explained within computational uncertainty of the used method?

The percentage values do not have a quantitative meaning, the percentage values has been computed in relation to the parent ion intensity and presented only for better understanding while reading the spectra.

60. In Figure 8 caption, it can be rephrased as “Mass spectra of the reactions between the neutral reagents (chloroform, bromoform, dichloromethane, and nitromethane) and the ion source generated fragments recorded with a For the collision energy (ECM) of each anion, please”

Corrected.

61. In conclusion Line 325, isn't it m/z 125 corresponding to the threshold energy of 245 kJ/mol?

No. There was mistake in main text. The proper values are added on figure and for m/z 99 is 245 kJ/mol.