Referee #6

The manuscript written by Kurzydym et al. explores the fragmentation pathways of an atmospherically important acid, Norpinonic acid (usually formed in the atmospheric oxidation process of α-pinene and other monoterpenes) which is a SOA component. The authors used tandem mass spectrometry technique and quantum chemical calculations to provide insight into the Norpinonic acid fragmentation pattern in the gas phase. I think the findings of the study are useful additions to the understanding of chemical structures of fragmentations from acids (here Norpinonic acid). However, I noticed some inconsistencies in numbers between the text and the figures in multiple places which I marked in the comments below. I recommend the manuscript for publishing in ACP after the following comments are addressed.

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?

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.

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?

Other comments:

4. In abstract Line 10, use subscript for "ozone (O_3)" instead of "*O3"*. Also, "In the present study, tandem …" instead of "*In the presented studies"*.

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

6. In Line 19, Please consider rephrasing and correcting as "Loss of C_3H_6O 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 C_2H_4O …."*

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 …"*

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.

9. On page 2 Line 33, it is not necessary to put the "dot" with OH and NO_3 radicals.

10. In Line 34, "result in the secondary organic aerosol (SOA) formation" instead of "*result with …"*

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

12. In Line 52, "However, to do the proper…" instead of "*However, to the proper ...."*

13. In Line 57, consider writing as "…… Norpinonic acid is considerably significant which is about 0.2-1.1 $ng.m^{-3}$"

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

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

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.

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

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

19. In Line 96, "In the present study ...." instead of "*In presented studies…*"

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

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

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

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"

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

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 $(H\text{-}C{=}C{=}O)^-$. It is missing one carbon atom with a C=C double bond.

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

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

28. In Line 145, refer to Fig. 5 here as "…. loss of the neutral molecule C_3H_6O (see Fig. 5 below), …."

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

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

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), …."

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), …."

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

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.

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

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?

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

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

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.

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

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.

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

43. In Line 208, write "in exothermic process" instead of "*on exothermically way*"

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

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?

46. In Line 217, replace the word "*intermediate*" with "isomer" before P_99B.

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

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.

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?

50. In Line 230, "show that" instead of "*shown, that*"

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?

52. In Line 245, "…. reaction with neutral species …"

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?

54. In Line 269, replace the word "*consulted*" by "compared"

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

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

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.

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%)?

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?

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 …."

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