Full product pattern recognition in thermal degradation of β-carotene through ionization enhancement

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Outline

Purpose:

- **Develop a rapid mass spectrometric method to study thermochemistry of solid chemical compounds and composition.**
- **Evaluate the degradation mechanisms, activation energies for bond broken and bond rearrangement, etc.**

Methods:

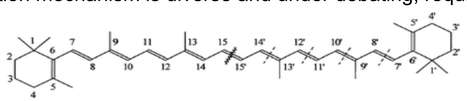
- **Atmospheric Solid Analysis Probe Mass Spectrometry (ASAP-MS) modulated by temperature, oxygen isotope, and solvent vapor molecules:**
  - **soft ionization for easy mass interpretation**
  - **simultaneous low energy collision fragmentation MS of a mixture of products**
  - **large range of temperature variation up to 600°C**

Results:

- **Temperature dependent full product patterns------thermodynamics and reaction mechanisms**
- **Solvent enhanced ionization selective for the radical processes**

Introduction

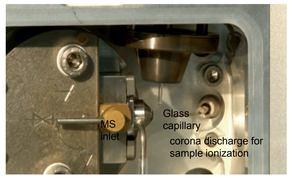
- 4S of mass spectrometry: **s**ensitive, **s**elective, **s**peed, and **s**imple
- ASAP-MS has been successfully applied to analyze the chemical mixtures in food, explosive, and drug, but not on their thermochemical properties.
- ASAP-MS has been applied to measure the vapor pressures and heats of sublimation of thermally stable solid organics.
- Pyrolysis-gas chromatography/MS (Py-GC/MS) is only able to identify volatile and semi-volatile products, not a full product pattern.
- Thermal degradation of β-carotene has been studied since early 60s', but still no full product pattern has been reported.
- The degradation mechanism is diverse and under debating, requiring more detailed studies.



Experimental

ASAP-MS modulated by temperature, oxygen isotope, and solvent vapor molecules:

1. attach carotene crystals onto the glass capillary,
2. Hot nitrogen gas was used to thermally evaporate and degrade carotenes,
3. Temperature dependent mass spectrometry was obtained with different temperature profiles,
4. Full product pattern was obtained at certain temperatures,
5. Oxygen isotope was used to verify oxygen involvements in thermal degradation reactions,
6. Input solvent molecules to verify ionization models,
7. Low energy collision fragmentation was used to identify the mixture and their structures.



ASAP-MS setup

Solvents: Hexane, dodecane, water, methanol

Take-home message

- Detailed degradation mechanisms for observed products: mass 457, 444, 430, 378, 346, etc.
- Origin of both even and odd number mass products and their structural relationships
- Temperature dependent full product patterns and selective ionization enhancement

Results and discussion

1. Temperature dependent full product pattern of thermal degradation of β-carotene

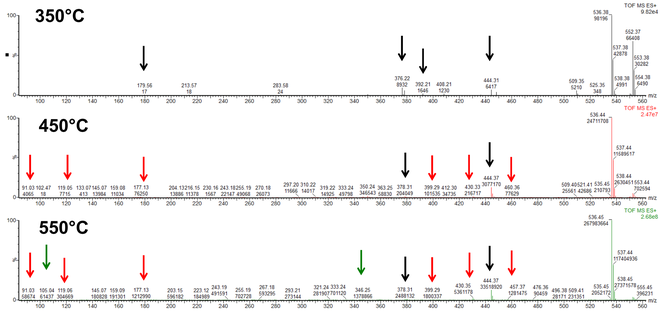


Fig.1. representative mass spectra of β-carotene thermal degradation at 350°C, 450°C, and 550°C. Arrows are pointed to (new) products being identified.

2. Thermodynamics of each products

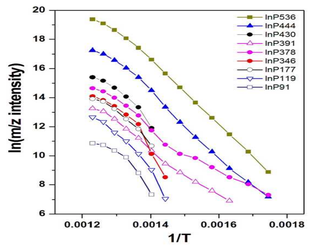


Fig. 2. Arrhenius plots of the identified products in comparison to β-carotene evaporation (mass 536).

3. Oxygen isotope effects

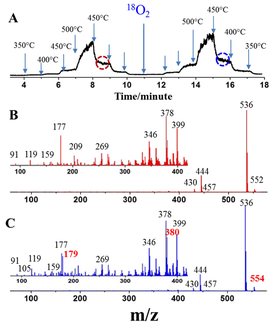


Fig. 3. oxygen effect on the full product patterns at 450°C.

4. Solvent induced ionization enhancements

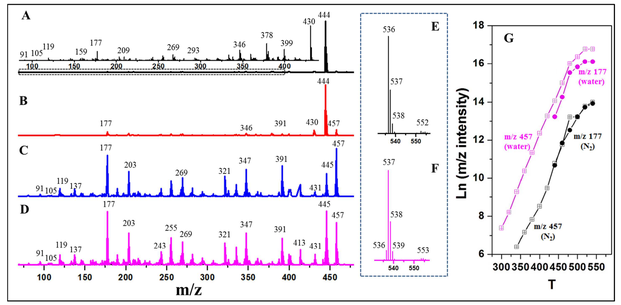
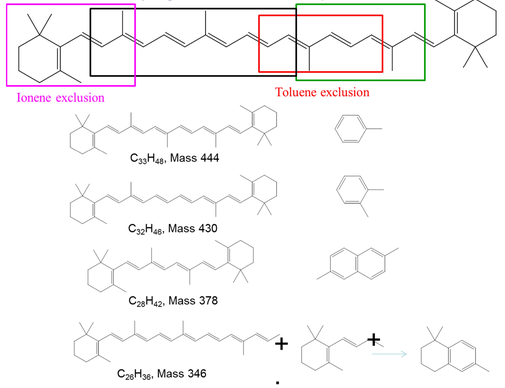


Fig. 4. ionization enhancement by solvent molecules. (A) N_2, (B) N_2+dodecane, (C) N_2+methanol, (D) N_2+water.

5. Proposed degradation mechanisms and corresponding products



Conclusions

1. **The full product pattern of thermal degradation of β-carotene has been observed and evaluated based on atmospheric solid analysis probe mass spectrometry.**
2. **Both volatile and nonvolatile chemical compounds are simultaneously detected, and the product pattern is temperature dependent.**
3. **Oxygen and solvent molecules are not readily involved in the decomposition processes.**
4. **In addition to mass 444 and 378 and masses for toluene, xylene, and dimethyl naphthalene, several more products are observed in real time.**
5. **Mass 430 is believed to be due to the exclusion of xylene.**
6. **Mass 346 appears at relatively higher temperature, and its intensity is significantly enhanced by the water and methanol molecules. It is proposed to be due to a direct breakdown of 9-10 and 9'-10' double bonds from charged radicals.**
7. **Mass 346 may be coincidently related to the formation of ionenes.**
8. **The full product pattern modulated by the solvent molecules confirms the radical processes that lead to odd number mass products which are thus enhanced by protic solvent molecules.**

Manuscript to be submitted

Acknowledgements

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