Investigation of the unimolecular reactions of nitro-substituted polycyclic aromatic hydrocarbons

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are speculated to constitute 20% of carbon in interstellar space. However, the nature of how these molecules are formed as well as their function in such an environment remains part of an ongoing area of research.

It has been theorized that PAH molecules may play an important role in interstellar space, such as the catalysis of H_2 formation and shielding organic reactions.[1] PAHs may also be involved in the formation of small molecules essential for life such as CO_2, O_2, H_2O, etc.

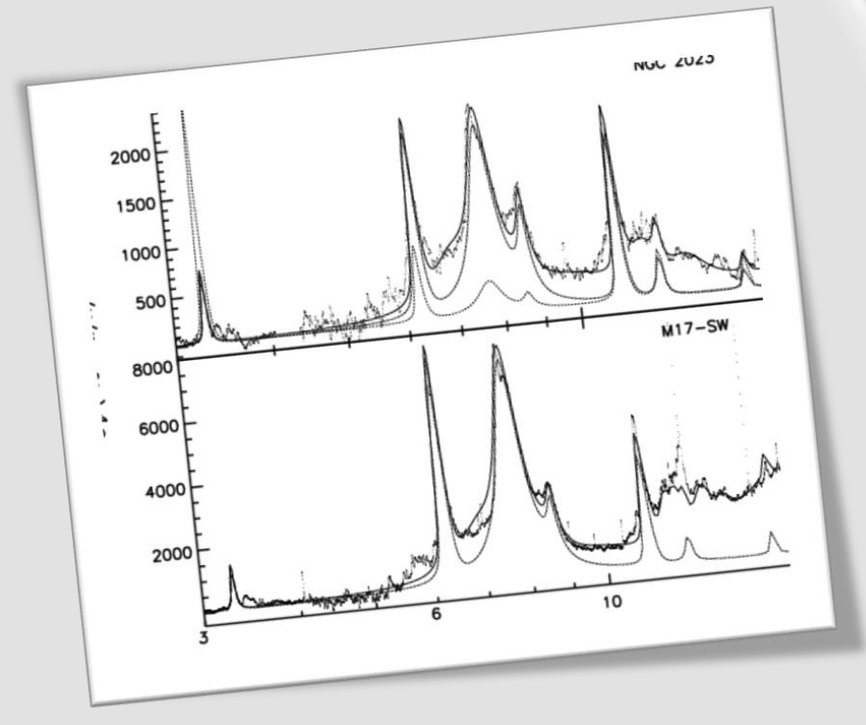


Figure 1. IR spectra emitted from gas-phase PAH molecules in interstellar space as a result of UV absorption

This experiment looks at the unimolecular reaction dynamics of nitro-substituted PAH molecules to elucidate their role in the interstellar medium by using atmospheric pressure chemical ionization (APCI) followed by a collision induced dissociation on a triple quadrupole mass spectrometer.

Methodology

Step 1: Collect Spectra

- Prepare PAH sample by making a dilute (~10-50 µg/mL) methanol solution
- Ionize sample using atmospheric pressure chemical ionization (APCI)
- Collect spectra at increasing kinetic energy within collision cell of triple quadrupole mass spectrometer

Step 2: Create Breakdown Diagram

- Using the spectra, construct a breakdown diagram by modelling relative abundance of products as a function of translational energy (E_{CM}) within the hexapole collision cell

Step 3: Calculate Vibrational Frequencies

- Calculate the vibrational frequencies of the ion using computational methods

Step 4: Fit a Curve to the Graph

- Fit a curve to the breakdown diagram by applying RRKM theory, using the calculated vibrational frequencies and $T_{CM} = T_i + \alpha E_{CM}$
- Collect thermodynamic information about ion based on the parameters used to produce curve.

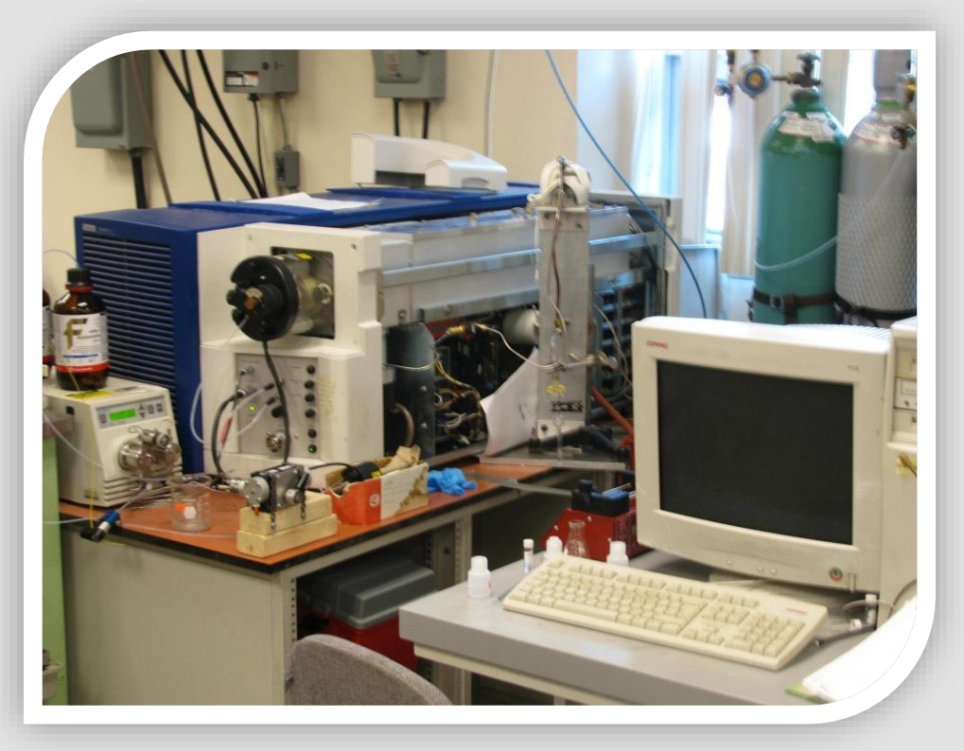


Figure 2. Micromass QuattroLC triple quadrupole mass spectrometer

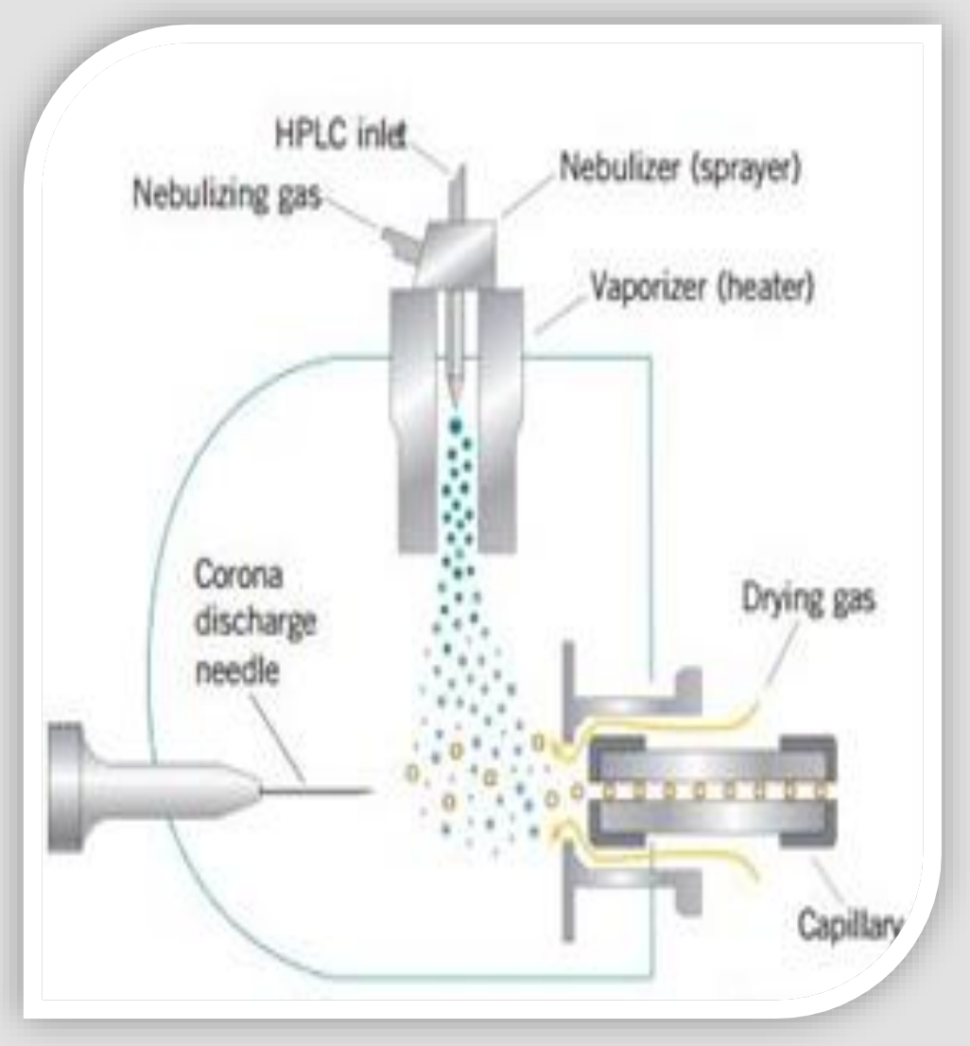


Figure 3. Schematic of an atmospheric pressure chemical ionization source

$$E_{\mathrm{CM}} = E_{\mathrm{LAB}}\left(\frac{m_{\mathrm{Ar}}}{m_{\mathrm{Ar}} + m_{\mathrm{ion}}}\right)$$

Figure 4. Equation to convert from lab frame to centre of mass frame energy

$$P(E, E_{\mathrm{CM}}) = \frac{\rho(E)\mathrm{e}^{-E/RT_{\mathrm{CM}}}}{Q(E_{\mathrm{CM}})}$$

Figure 5. Post-collision internal energy distribution

$$k(E) = \frac{\sigma N^{\ddagger}(E - E_0)}{h\rho(E)}$$

Figure 6. Calculation of microcanonical rate constant using RRKM theory

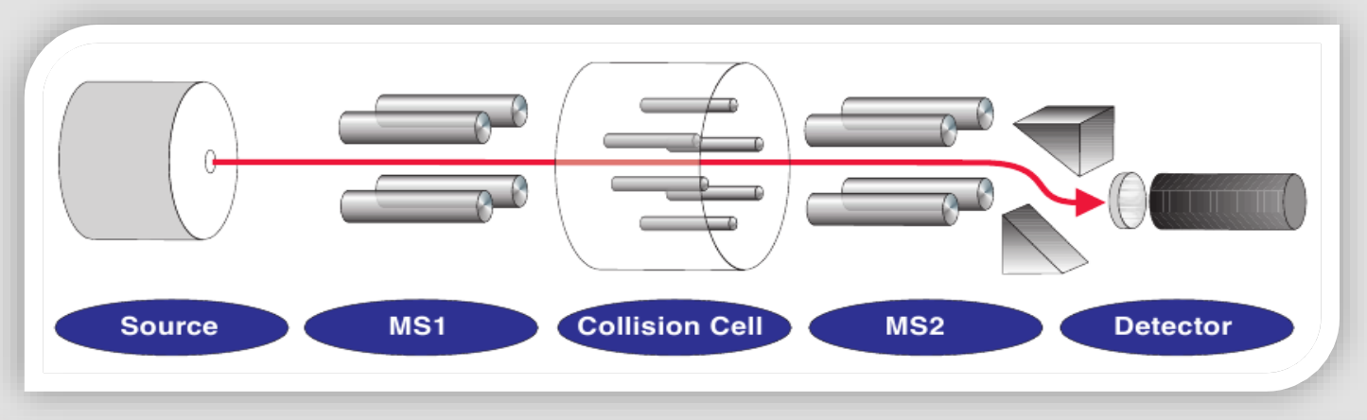
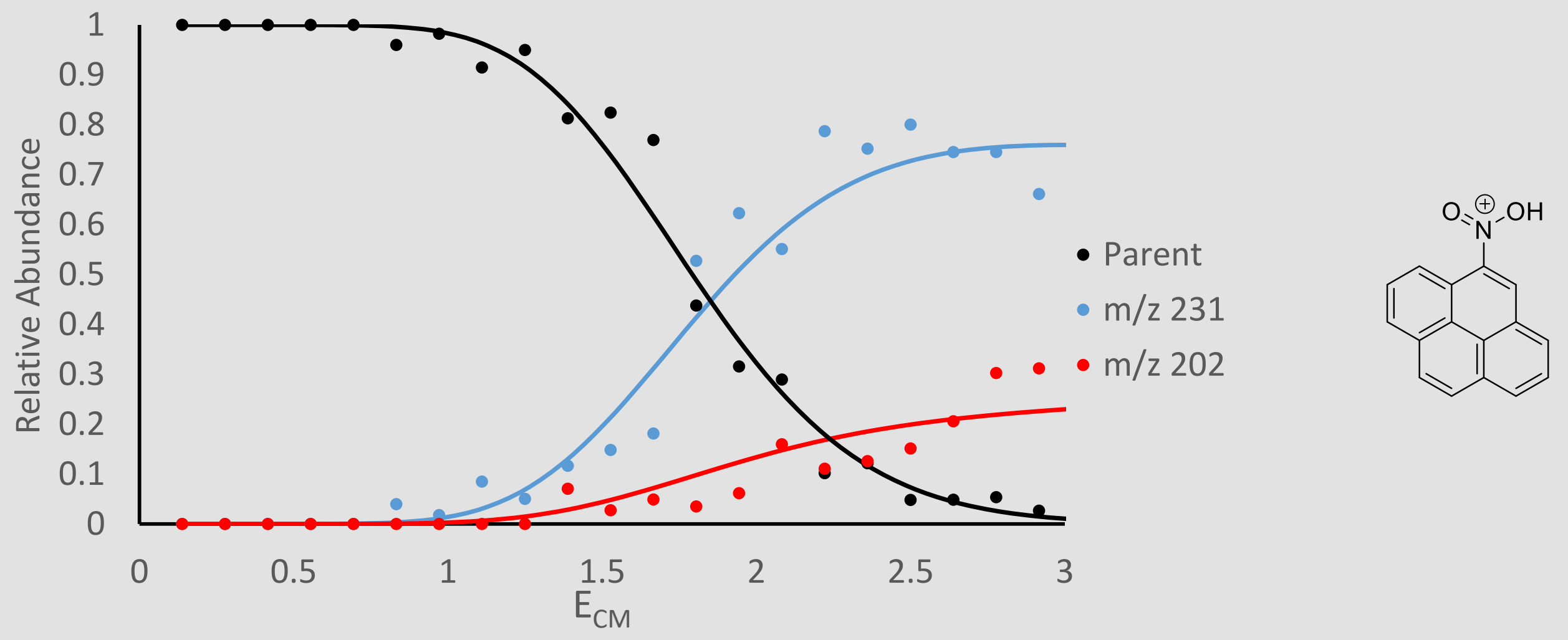


Figure 7. Basic schematic of a triple quadrupole mass spectrometer

Results

A two channel system where there was either a loss of NO_2 or OH from the parent ion was observed in all species with the exception of 9-nitroanthracene in which case there was only a loss of OH. The dominating channel in the two-channel systems was the loss of OH from the protonated species.

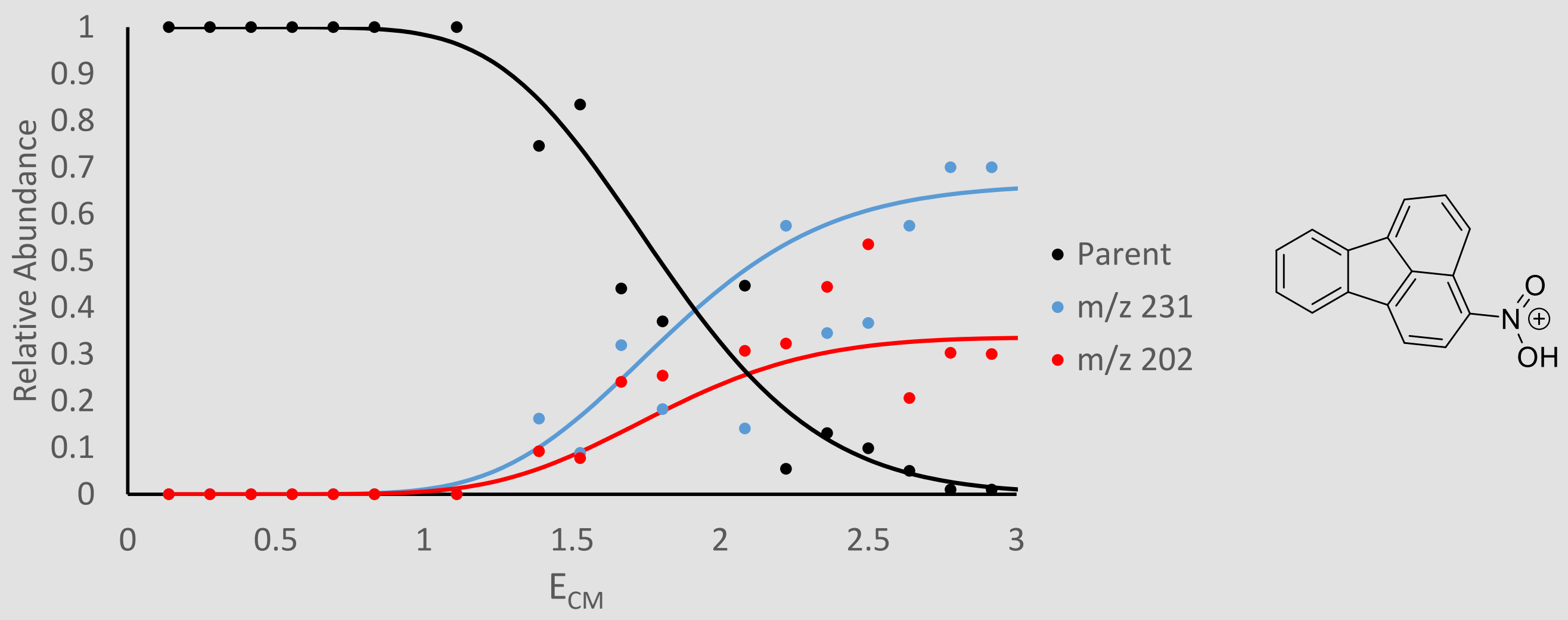
1-Nitropyrene



Reaction 1A: $C_{16}H_9NO_2H^+ \rightarrow C_{16}H_9NO^+ + OH$

Reaction 1B: $C_{16}H_9NO_2H^+ \rightarrow C_{16}H_{10}{}^+ + NO_2$

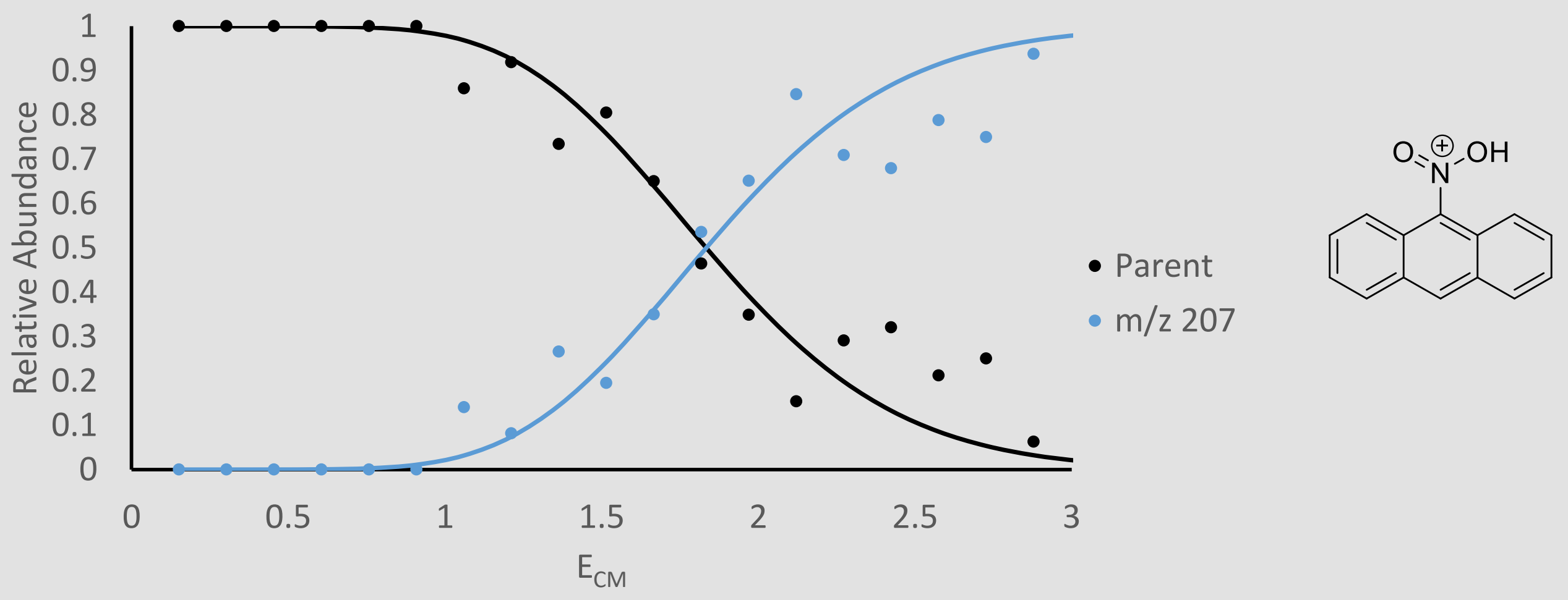
3-Nitrofluoranthene



Reaction 2A: $C_{16}H_9NO_2H^+ \rightarrow C_{16}H_9NO^+ + OH$

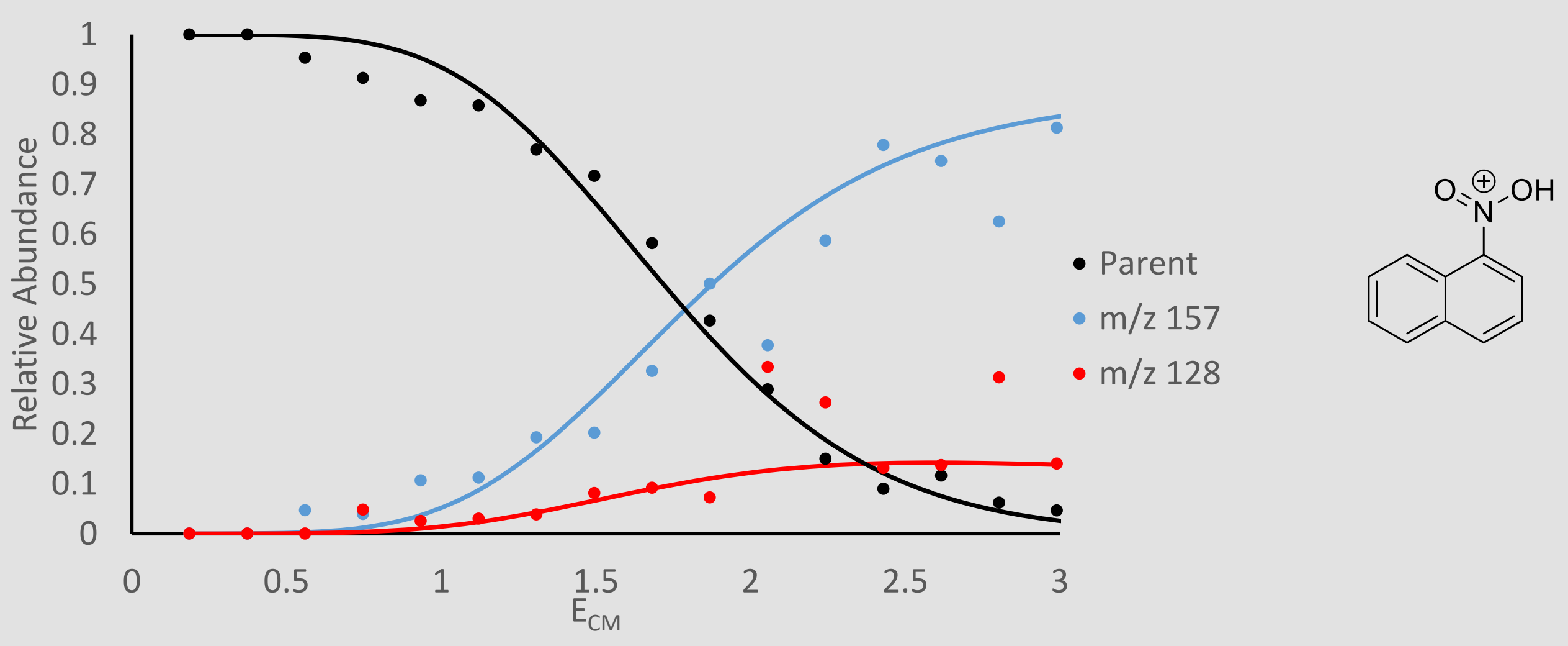
Reaction 2B: $C_{16}H_9NO_2H^+ \rightarrow C_{16}H_{10}{}^+ + NO_2$

9-Nitroanthracene



Reaction 3: $C_{14}H_9NO_2H^+ \rightarrow C_{14}H_9NO^+ + OH$

1-Nitronaphthalene



Reaction 4A: $C_{10}H_7NO_2H^+ \rightarrow C_{10}H_7NO^+ + OH$

Reaction 4B: $C_{10}H_7NO_2H^+ \rightarrow C_{10}H_8{}^+ + NO_2$

Figure 8. Breakdown diagrams of nitro-substituted polycyclic aromatic hydrocarbons. Data was collected using a triple quadrupole mass spectrometer in a collision induced dissociation (CID), performed in a hexapole collision cell at a pressure of about 1.4×10^{-3} mbar, and ionized using atmospheric pressure chemical ionization (APCI). The probe temperature was set to 400 K.

Table 1. Unimolecular reactions of nitro-substituted PAH molecules and the associated thermodynamic parameters determined experimentally in a collision induced dissociation

Reaction	E_0 (eV)	ΔS‡ ($J \cdot mol^{-1} \cdot K^{-1}$)	α
1A	1.70 ± 0.05	7 ± 3	270 ± 10
1B	1.75 ± 0.05	2 ± 2	270 ± 10
2A	1.80	15	270
2B	1.75	7	270
3	1.15 ± 0.10	7 ± 8	220 ± 20
4A	1.40 ± 0.10	17 ± 3	230 ± 20
4B	1.40 ± 0.10	1 ± 2	230 ± 20

Discussion

Trends in Activation Energy?

In the collision induced dissociation experiment, the ionized nitro-substituted PAH molecules were found to dissociate at very low energies compared to non-substituted PAH molecules. Ionized PAH molecules as small as benzene experience H-loss at a critical energy of 4.62 eV, compared to the highest activation energy observed in this experiment of 1.80 eV for the 3-nitrofluoranthene ion[2]. The lower activation energy for these nitro-substituted PAH molecules suggests that the nitro substituent destabilizes the molecule. As a result, it is more favourable to lose the substituent, or parts of the substituent, at lower energies than to lose a hydrogen in a non-substituted PAHs. Competing channels for the same ion were observed to have similar activation energies with small relative error (about 8% at most).

Trends in Activation Entropy?

Further, the entropy of activation is indicative of the change in entropy from the parent ion to the transition state. Therefore, the channel with the higher ΔS‡ will be the most entropically favoured reaction pathway. Because competing channels in all the reactions have an approximately equal activation energy, the dominant channel will be highly dependent upon the entropy of activation. It is therefore apparent from the experimental data that the dominating channel (loss of hydroxyl radical) should have the highest activation entropy and that was confirmed by the results in which the activation entropy of the channel with loss of OH was generally higher by about 5 J/(mol K) than the channel with a loss of NO_2. The loss of NO_2 was not observed in 9-nitroanthracene most likely due to the fact that there is not an adjacent free carbon to the nitro group to promote this loss.

Astrophysical Impacts

In the 1960s the hydroxyl radical was detected in the interstellar medium[3]. If nitro-substituted PAHs such as the ones studied in this experiment are present in the interstellar medium, it is possible that they could be a source of these hydroxyl radicals. Hydroxyl radicals can react with many hydrocarbons such as ethane and alcohols such as methanol to form water at 298 K, so it is possible this may happen as well in the gas phase in the interstellar medium[4, 5].

References

1. *PAHs and the universe: A symposium to celebrate the 25th anniversary of the pah hypothesis*; Joblin, C.; Tielens, A. G. G. M., Eds.; EAS Publications Series, **2011**; Vol. 46.
2. Jochims, H. W.; Ruhl, E.; Baumgartel, H.; Tobita, S.; Leach, S. *Astrophysical Journal* **1994**, *420*, 307–317.
3. *Interstellar Molecules: Their Laboratory and Interstellar Habitat*; Yamada, K., Winniwiser, G., Eds.; Springer: Berlin, 2011.
4. Atkinson, R. *Chem. Rev.* **1986**, *86*.
5. J. A. Manion, R. E. Huie, R. D. Levin, D. R. Burgess Jr., V. L. Orkin, W. Tsang, W. S. McGivern, J. W. Hudgens, V. D. Knyazev, D. B. Atkinson, E. Chai, A. M. Tereza, C.-Y. Lin, T. C. Allison, W. G. Mallard, F. Westley, J. T. Herron, R. F. Hampson, and D. H. Frizzell, NIST Chemical Kinetics Database, NIST Standard Reference Database 17, Version 7.0 (Web Version), Release 1.6.8, Data version 2015.12, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899-8320. Web address: http://kinetics.nist.gov/

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