



What do we expect from the dissociation of ionized nitro-substituted polycyclic aromatic hydrocarbons in the interstellar medium?

Jake Burner, Brandi West, Paul M. Mayer*

Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa K1N 6N5, Canada



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ABSTRACT

The unimolecular dissociations of four nitro-substituted polycyclic aromatic hydrocarbon (PAH) ions were explored using tandem mass spectrometry, imaging photoelectron photoion coincidence (iPEPICO) spectroscopy and computational chemistry. Ionized 1-nitronaphthalene and 9-nitroanthracene both exhibit the loss of C_2O_2 (likely sequential loss of two CO molecules), NO and CO_2 as primary fragmentation channels, while for the larger 3-nitrofluoranthene and 1-nitropyrene ions CO_2 loss is replaced by NO_2 loss. The reaction pathways for 1-nitropyrene ions were calculated at the CCSD/6-31G(d)//B3-LYP/6-31G(d) level of theory. NO loss is preceded by a nitro-to-nitrite isomerization requiring 2.09 eV, while NO_2 loss was found to form the triplet state [pyrene - H]⁺ ion (requiring 2.36 eV), consistent with the behavior of this class of PAH ions. iPEPICO-derived energies for these two reactions are in excellent agreement with theory, 2.05 ± 0.09 eV and 2.38 ± 0.12 eV, respectively. The iPEPICO-derived reaction energy for C_2O_2 loss is 2.76 ± 0.08 eV, but we were unable to calculate this reaction pathway. The most energetically-favorable products of sequential CO loss lie 3.2 eV and 2.05 eV, respectively, lower in energy than the precursor ion, indicating that what was measured was an effective barrier height for this reaction.

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1. Introduction

Ionized and neutral polycyclic aromatic hydrocarbons (PAHs) are speculated to constitute approximately 20% of the carbon in interstellar space. These species are also suspected to be involved in important chemical events in the interstellar medium (ISM) such as H_2 -formation catalysis and in shielding organic reactions from high energy radiation [1]. However, the nature of how these molecules are formed, as well as their function in such environments, remain part of ongoing research. This work focuses primarily on the dissociation of nitrated PAH ions and more specifically, ionized 1-nitropyrene.

PAHs absorb UV light from stars which can initiate photodissociation and decrease their presence in astrophysical environments. Therefore, while nitrated PAH ions have not been observed in the ISM, nitrogen-containing products from their dissociation have been detected and could suggest the presence of nitrated PAHs. Nitrogen-containing PAHs have been spectroscopically observed in the ISM and are possible building blocks for nitrogen-containing polycyclic aromatics, such as purines, for the synthesis of the

nucleic acids essential for life [2]. Furthermore, nitric oxide, a dissociation product common to all nitrated PAH ions investigated in this work, has been detected in the ISM, specifically in the dark cloud L134 N [3].

Nitrated PAHs also have been observed in the atmosphere as products of diesel and gasoline combustion [4]. They have been found to be formed mainly from the reactions of PAHs with hydroxyl radicals and NO_x gases. They pose environmental concern as nitrated PAHs are known potent carcinogens and mutagens and contribute significantly to air pollution. Moreover, substituted PAHs generally have a lower volatility than PAHs and therefore are more likely to be deposited on fine particles in the air which are taken easily into the human body [5].

In the present study, we investigated the unimolecular reaction dynamics of ionized 1-nitronaphthalene, 9-nitroanthracene, 3-nitrofluoranthene, and 1-nitropyrene by collision-induced dissociation (CID) mass spectrometry to establish trends in the ion chemistry as a function of PAH size. The pathways and energetics for the unimolecular reactions of ionized 1-nitropyrene were explored computationally at the CCSD/6-31G(d)//B3-LYP/6-31G(d) level of theory and experimentally with imaging photoelectron photoion coincidence (iPEPICO) spectroscopy as an approximation for larger nitro-PAHs expected to play a role in the ISM.

* Corresponding author.

E-mail address: pmmayer@uottawa.ca (P.M. Mayer).

2. Experimental procedures

1-Nitronaphthalene, 9-nitroanthracene, 3-nitrofluoranthene, and 1-nitropyrene were purchased from Sigma-Aldrich (Sigma-Aldrich, Oakville, Ontario, CA), and used without further purification (each was >98% purity).

2.1. Tandem mass spectrometry

Atmospheric pressure chemical ionization (APCI) CID experiments were performed on a Micromass Quattro LC (Waters Micromass, Manchester, U.K.) triple quadrupole mass spectrometer equipped with a Z-spray source. Compounds were dissolved in chlorobenzene to produce a 100 $\mu\text{g mL}^{-1}$ solution [6]. This solution was delivered to the APCI source by syringe pump at a flow rate of 0.25 mL min^{-1} . The source block temperature was set at 80 °C while the probe temperature was kept at 400 °C. The corona and cone voltages were held at 4.0 kV and 30 V, respectively. The quadrupole resolution was set to 18 in the Masslynx software to provide baseline separation of all mass spectral peaks. CID was carried out using argon collision gas (pressure of $\sim 10^{-3}$ mbar, see figure captions for specific pressures used for each ion) and over a laboratory-frame collision energy range (E_{lab}) of 0–30 eV.

2.2. iPEPICO

iPEPICO spectroscopy experiments were conducted on the VUV beamline at the Swiss Light Source (SLS, Paul Scherrer Institut, Villigen, Switzerland) and have been described in detail elsewhere [7–9]. However, in the current study, the ion optics were adjusted for space-focusing, and thus higher mass resolution, rather than ion imaging. 1-nitropyrene was thermally volatilized into the photon interaction region with a heated oven and photoionized by monochromatic synchrotron radiation (4–8 meV resolution depending on the photon energy) [10]. Electrostatic lenses direct the ions toward a time-of-flight (TOF) mass spectrometer, while the ejected electrons are velocity-mapped on an imaging multichannel plate (MCP) detector. The electrons are time- and position-stamped at the detector and the corresponding photoions are detected in delayed coincidence. Threshold electrons account for the majority of the signal at the center of the MCP, whereas non-zero-kinetic energy electrons are mostly detected according to their off-axis momentum. Some of the non-zero-kinetic energy electrons will have the proper trajectory to hit the center spot, therefore the mass spectrum based on electrons detected in a ring around the center spot is used to account for this contamination. The ring signal can then be subtracted from the center signal to obtain the threshold photoionization mass spectrum [11]. The photon energy range used was 10.95–13.05 eV, with data points taken every 0.05 eV.

The TOF mass spectrometer consists of two acceleration regions, one with a low draw out potential that allows ions dissociating on the microsecond time scale to do so while being accelerated. The result is asymmetric time-of-flight peaks for product ions, which can be modeled to extract unimolecular decay rate constants as a function of photon energy. When multiple product ions are generated, they are all formed with the same overall effective decomposition rate constant of the precursor ion, and the fractional fragment ion abundances, i.e., the branching ratios, can be used to apportion absolute dissociation rates to each of the decay channels. This way, dissociation rate constants are obtained for all channels on the basis of the asymmetric peak profile of just one fragment ion.

The mass-selected threshold photoelectron spectrum (TPES) of 1-nitropyrene was acquired from 7.40 to 8.04 eV (0.002 eV steps) to establish the ionization energy (Fig. S1). The TPES exhibits a strong, narrow, primary ionization peak which means the verti-

cal and adiabatic ionization energies (IE_a) are essentially the same at 7.86 ± 0.01 eV. This value was used to convert photon energies to ion internal energies for kinetic modeling. The TPES exhibits vibrational structure assigned to a strong in-plane deformation coupled with symmetric NO_2 stretch calculated at 1337 cm^{-1} at the B3-LYP/6-31G(d) level of theory.

2.3. Computational procedures

Geometry optimizations and harmonic vibrational frequency calculations of all species and transition states were conducted using the Gaussian 09 package [12] at the B3-LYP/6-31G(d) level of theory. Transition states were confirmed with the intrinsic reaction coordinate (IRC) protocol. CCSD/6-31G(d) single point energy calculations were carried out on the B3-LYP structures.

The minimalPEPICO program was used to fit the iPEPICO experimental breakdown diagrams and TOF distributions [9]. In short, the program combines the physical parameters of the iPEPICO experimental set up at the SLS with temperature (390 K in the current experiment, for the initial neutral molecule internal energy distribution) and the rate constant for each pathway to calculate theoretical branching ratios and fragment ion time-of-flight distributions for the ion dissociation as a function of photon energy, which are then compared to the experimental breakdown curves and asymmetric fragment ion TOF peaks, where applicable. Rice-Ramsperger-Kassel-Marcus (RRKM) theory was used to calculate $k(E)$ according to Eq. (1) [13,14],

$$k(E) = \frac{\sigma N^\ddagger(E - E_0)}{h\rho(E)} \quad (1)$$

where σ represents the reaction degeneracy, h is Planck's constant, $N^\ddagger(E - E_0)$ is the number of internal states for the transition state at internal energy ($E - E_0$) and $\rho(E)$ is the density of states for the reactant ion at internal energy (E). For nitropyrene, σ values of 2, 1, and 2 were used for NO , NO_2 , and C_2O_2 loss, respectively, based on the number of oxygen atoms available to participate in the reactions. Ro-vib densities and sums-of-states were calculated using B3-LYP/6-31G(d) rotational constants and harmonic vibrational frequencies by the direct count algorithm of Beyer and Swinehart [15]. The reaction pathways leading to loss of NO_2 and C_2O_2 lacked calculated transition state structures, and so the $N^\ddagger(E - E_0)$'s for these reactions were evaluated by approximating the transition state vibrational frequencies and rotational constants with those of the precursor ion, less one vibrational mode to represent the reaction coordinate. For example, in the case of NO_2 loss, a C–N stretching mode was removed. Of the remaining $3N - 7$ (N = number of atoms) modes for the transition state, the lowest five frequencies were scaled to adjust the entropy of activation. Factors less than one increase $\Delta^\ddagger S$ while values greater than one decrease $\Delta^\ddagger S$ [14]. The agreement between the experimental and theoretical breakdown curves was achieved by varying E_0 and $\Delta^\ddagger S$ for the three reactions. Error bars were established by finding the limits in E_0 and $\Delta^\ddagger S$ that resulted in acceptable fits to the experimental data, which means a value of < 0.1% for Eq. (2)

$$\text{Difference} = 1 - \frac{\Sigma((\text{Expt})(\text{Calc}))}{\sqrt{(\Sigma((\text{Expt})(\text{Expt}))\Sigma((\text{Calc})(\text{Calc}))}} \quad (2)$$

where *Expt* and *Calc* refer to the experimental and calculated relative ion abundances in the breakdown curves, respectively.

Full details for the APCI-CID model have been reported previously [16,17]. In addition to the instrumental parameters defining the timescale of the experiment and the RRKM $k(E)$, the post-collision internal energy distribution of the dissociating ions is

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