Hydroxy-Substituted Polycyclic Aromatic Hydrocarbon Ions as Sources of
CO and HCO in the Interstellar Medium

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ABSTRACT: Tandem mass spectrometry was used to explore the trends in the unimolecular fragmentation of the ionized hydroxy-substituted polycyclic aromatic hydrocarbons 1-naphthol, 9-hydroxyphenanthrene and 1-hydroxypyrene. The main dissociation reactions across all ring systems were CO- and HCO-loss, with ionized 1-naphthol also losing H atoms. Both ionized 1-naphthol and 9-hydroxyphenanthrene displayed the sequential loss of C₂H₂ and C₄H₂ from the [M-HCO]⁺ ions, reminiscent of unsubstituted PAH ions. CO-loss is slightly favored for 1-naphthol and 9-hydroxyphenanthrene at low collision energy, but less so for 1-hydroxypyrene. Reaction mechanisms for HCO- and CO-losses from 1-hydroxypyrene were derived from CCSD/6-31G(d)//B3-LYP/6-31G(d) calculations. The CO-loss mechanism is dominated by two transition states, TS-A governing a 1,3-H shift in the molecular ion, and TS-C which governs a ring-closing step to form a five-member ring in the product ion. HCO-loss occurs over a much flatter potential energy surface with the intermediate being the product ion bound to the carbon atom of HCO. Imaging photoelectron photoion coincidence spectroscopy of 1-hydroxypyrene yielded threshold photon-energy resolved breakdown curves and time-of-flight distributions that were modeled with RRKM theory to give 0 K reaction energies for HCO- and CO-losses of 3.92 ± 0.05 and 2.91 ± 0.05 eV, respectively. The entropy of activation for the two channels were very different, 14 and 95 JK⁻¹mol⁻¹, respectively, a result consistent with the calculated mechanisms. The threshold photoelectron spectrum yielded an IE value of 7.14 ± 0.01 eV for 1-hydroxypyrene.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are suggested to comprise approximately 20% of carbon in the interstellar medium (ISM).^{1,2} Existing as both neutrals and ions, they are thought to participate in H₂ formation and in the shielding of other chemical reactions from cosmic radiation.² PAHs in the ISM can be sources of important molecular building blocks upon photodissociation by UV light. An open question is whether functional forms of these species, such as hydroxy-PAHs, produce small molecules such as H₂O, CO or HCO, the building blocks of molecules like amino acids. A review on extraterrestrial organic matter reported the presence of a wide variety of O-containing species including CO and HCO.³ A computational study by Sadjadi and co-workers demonstrated that the 11.3 micron IR band was likely not due to PAHs, but substituted PAHs, including oxygen-containing species.⁴ In separate laboratory studies, Gudipati and Yang,⁵ Cook et al.⁶ and Hardegree-Ullman and co-workers⁷ found that oxygenated and hydroxylated PAHs were produced when PAHs embedded in astrophysical ices were irradiated by UV radiation.

In order to completely understand the photo-processing of PAHs in the ISM, it is necessary to unravel their competing unimolecular reactions. This work centers on the unimolecular reactions of small hydroxy-substituted PAH ions, especially the 1-hydroxypyrene radical cation, as prototypes for large hydroxy-substituted PAH ions in the ISM.

EXPERIMENTAL SECTION

1-hydroxynaphthalene (1-naphthol), 9-hydroxyphenanthrene, and 1-hydroxypyrene were purchased from Sigma-Aldrich (Sigma-Aldrich, Oakville, ON, CA, >97% purity) and used without further purification.

TANDEM MASS SPECTROMETRY

Atmospheric pressure chemical ionization (APCI) experiments were performed with a Micromass Quattro LC (Waters Micromass, Manchester, U.K.) triple quadrupole mass spectrometer. A syringe pump was used to deliver 100 $\mu\text{g mL}^{-1}$ solutions of each compound in chlorobenzene⁸ to the APCI source at a flow rate of 0.25 mL min⁻¹. The source block and probe temperatures were set at 80 °C and 400 °C, respectively, while corona and cone voltages were set to 4.0 kV and 40 V. Baseline separation of the peaks in the mass spectra was achieved by setting the quadrupole resolution to 18 in the Masslynx software. Collision-induced dissociation (CID) was carried out using argon as a collision gas at a pressure of approximately 8×10^{-4} mbar at intervals of 1 eV laboratory-frame collision energy (E_{lab}). These collision energies were then converted to the centre-of-mass frame (E_{COM}) before plotting.

iPEPICO

iPEPICO spectroscopy experiments were conducted on the VUV beamline at the Swiss Light Source (SLS, Paul Scherrer Institut, Villigen, Switzerland) and have been previously described;⁹⁻¹¹ however the ion optics were adjusted for space-focusing rather than ion imaging for higher mass resolution. 1-hydroxypyrene was introduced into the photon interaction region with a heated

oven set to 93°C and photoionized by monochromatic synchrotron radiation (4–8 meV resolution).¹² Ejected electrons are velocity-mapped on an imaging multichannel plate (MCP) detector, and time- and position-stamped. The corresponding photoions are directed toward a time-of-flight (TOF) mass spectrometer with an electrostatic lens assembly and detected in delayed coincidence. Threshold electrons are preferentially detected at the center of the MCP, whereas non-zero-kinetic energy electrons are mostly detected off this axis. To account for the non-zero-kinetic energy electrons that hit the center spot, the mass spectrum based on electrons detected in a ring around the center spot is subtracted, yielding the threshold photoionization mass spectrum.¹³

The TOF mass spectrometer has two acceleration regions, the first with a low draw out potential. Ions dissociating on the microsecond time scale can do so in this region, resulting in asymmetric time-of-flight peaks. These peaks can be modelled to extract unimolecular decay rate constants.¹¹ All product ions are formed with the same effective decomposition rate constant of the precursor, and so the asymmetric peak profile of just one fragment ion can yield the dissociation rate constant.

The ionization energy (IE) of 1-hydroxypyrene was determined from its mass-selected threshold photoelectron spectrum (TPES) to be 7.14 ± 0.01 eV, the first determination of this quantity. This value was used to convert between photon and ion-internal energies for kinetic modeling.

Figure 1. Mass-selected threshold photoelectron spectrum of 1-hydroxypyrene. Acquired from 7.0 – 7.7 eV (0.002 eV steps).

COMPUTATIONAL METHODS

Density functional theory calculations at the B3-LYP/6-31G(d) level of theory were employed for geometry optimizations and harmonic vibrational frequency calculations of all species using the Gaussian 16 suite of programs.¹⁴ Transition states were confirmed with the intrinsic reaction coordinate (IRC) method. CCSD/6-31G(d) single-point energy calculations were carried out on the optimized structures for comparison.

The minimalPEPICO program was used to model the iPEPICO breakdown curves and TOF distributions.¹¹ The program combines instrumental parameters with the initial neutral molecule internal energy distribution (based on the sample temperature) and the $k(E)$ for each dissociation pathway to calculate theoretical breakdown curves and TOF distributions which can be compared to the experimental data. Microcanonical $k(E)$ values were calculated according to Rice-Ramsperger-Kassel-Marcus (RRKM) theory, equation 1:^{15,16}

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

where σ is 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) . A σ value of 1 was used for both CO- and HCO-loss. Rotational-vibrational sums and densities of states were calculated by the direct count algorithm of Beyer and Swinehart¹⁷ employing B3-LYP/6-31G(d) rotational constants and harmonic vibrational frequencies. The transition state vibrational frequencies and rotational constants were taken from the calculated transition states in the reaction mechanisms, but then adjusted to achieve agreement between theory and experiment. When adjustments were necessary, the lowest five frequencies were multiplied by a common factor to change the entropy of activation (factors < 1 raise $\Delta^\ddagger S$ while factors > 1 drop $\Delta^\ddagger S$).¹⁶ E_0 and $\Delta^\ddagger S$ for each reaction were methodically adjusted until equation 2 had a value of $< 0.1\%$. Error bars were determined by loosening the limit for equation 2 to 1%.

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

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

RESULTS AND DISCUSSION

COLLISION-INDUCED DISSOCIATION

The CID breakdown curves for the three hydroxy-PAHs are found in Figure 2.

Figure 2. Collision-induced dissociation breakdown curves for ionized a) 1-naphthol, b) 9-hydroxyphenanthrene and c) 1-hydroxypyrene. See experimental procedures for details.

All three exhibit competitive loss of CO and HCO (28 and 29 Da, respectively), while 1-naphthol also shows H atom loss. 1-naphthol and 9-hydroxyphenanthrene also exhibit the loss of C₂H₂ and C₄H₂ (26 and 50 Da, respectively) from the [M-HCO]⁺ ion at high collision energy. In contrast to amino- and methyl-PAHs,^{18,19} H-loss does not dominate as ring-size increases, but rather the opposite, with 1-hydroxypyrene ions displaying no H-atom loss. Loss of 28 Da could also be due to C₂H₄, but the energy calculated for this reaction was much too high to be competitive.

COMPUTED REACTION MECHANISMS

Figures 3 and 4 show the lowest-energy pathways to CO- and HCO-loss from ionized 1-hydroxypyrene, respectively, calculated at the B3-LYP/6-31G(d) level of theory, together with the results of CCSD/6-31G(d) single-point energy calculations. CO-loss is initiated by a 1,2-H shift from the hydroxyl group to the adjacent ring carbon atom (TS **A**). The ring then opens to form a low-energy intermediate **B**, prior to having to overcome a large barrier (TS **C**) needed to close the five-member ring, leaving a low energy product ion complexed to CO. The CH₂ moiety in TS **C** is not co-planar with the rest of the ring since doing so would break the sp² character of the carbon atom and decrease delocalization of the unpaired electron. A higher energy product was identified as an ethenyl-phenalene isomer. Ionized 1-naphthol was found to follow analogous pathways (Figure S1, supporting information) suggesting these reactions are similar across the hydroxyPAHs, as was found for C₂H₂ loss for a wide range of unsubstituted PAH ions.²⁰

Figure 3. Reaction pathways (including ZPE) to CO-loss from ionized 1-hydroxypyrene calculated at the B3-LYP/6-31G(d) (—) and CCSD/6-31G(d)// B3-LYP/6-31G(d) (- - -) levels of theory.

In contrast, HCO-loss occurs on a “flatter” potential energy surface dominated by shallow wells and high energy intermediates between TS **A'** and **B'**, and following **C'**. The initial H-atom migration is a 1,2-H shift to the ring carbon (TS **A'**) followed by facile ring-opening to a high-energy intermediate **B'**. Ring-closing takes place to form a HCO-substituted ion **C'**, which then dissociates to the product ion.

Figure 4. Reaction pathway (including ZPE) to HCO loss from ionized 1-hydroxypyrene calculated at the B3-LYP/6-31G(d) (—) and CCSD/6-31G(d)// B3-LYP/6-31G(d) (---) levels of theory.

The RRKM $k(E)$ curves were calculated for the key reactions (R1-R3) in the CO-loss mechanism

and are shown in Fig. 5:

The large rate constant for $R2$ means that a two-well potential model is needed to determine the net rate constant for CO-production, which is also shown in Fig. 5.²¹ The $k(E)$ curve for HCO-loss, Figure 5, was calculated employing the vibrational frequencies of the final transition state prior to the formation of the ion-molecule complex in Figure 4 as an approximation of the net reaction. The experimental CID data shows CO-loss being outcompeted by HCO-loss with increasing excitation energy, and thus the former reaction should be associated with the lower $\Delta^\ddagger S$. To simulate the observed competition between CO- and HCO-loss, the $\Delta^\ddagger S$ of the HCO-loss channel was adjusted upwards until its $k(E)$ curve crossed with that for the net CO-loss reaction, leading to a $\Delta^\ddagger S$ value of $100 \text{ J K}^{-1} \text{ mol}^{-1}$. While large, it illustrates that the HCO-loss mechanism is mediated by entropically-looser structures than that for CO-loss. It also highlights that adjustments to the calculated surface will inevitably be made when a complex surface is approximated by a simpler kinetic model.

Figure 5. RRKM $\log_{10} k(E)$ curves for reactions 1-3, the net CO-loss reaction from a two-well model and two net $k(E)$ curves for HCO-loss with different $\Delta^\ddagger S$ values.

Imaging photoelectron-photoion coincidence spectroscopy. CID mass spectrometry is useful to examine the trends in reactivity of the hydroxy-substituted PAH ions; however, an ill-defined post-collision internal energy distribution means it is difficult to extract quantitative information. Accurate reaction energies for 1-hydroxypyrene were derived from iPEPICO spectroscopy. The asymmetry of the CO- and HCO-loss product ion peaks made it challenging to resolve their branching ratio. The IGOR PRO 4 (WaveMetrics, Lake Oswego, OR) software package was used to simulate the two asymmetric peaks and through spectral subtraction arrive at the branching ratio needed to generate the breakdown graph in Figure 6. There was significant uncertainty in

the branching ratio determination, and thus RRKM modeling focused more on the time-of-flight distributions themselves, Figure 7. A single transition state model was used for both CO- and HCO-loss pathways when using the minimalpepico software to model the iPEPICO data, with the $\Delta^\ddagger S_{600K}$ of the former adjusted to match that for k_{CO-net} in Figure 5. The resulting values for the two reaction energies and entropies are E_0 of 2.91 ± 0.05 eV and $\Delta^\ddagger S_{600K}$ of 14 ± 25 J mol⁻¹ K⁻¹ for CO-loss and E_0 of 3.92 ± 0.05 eV and $\Delta^\ddagger S_{600K}$ of 95 ± 25 J mol⁻¹ K⁻¹ for HCO-loss. The difference in $\Delta^\ddagger S$ for the two reactions is consistent with the RRKM analysis presented in Figure 5. The size of the hydroxypyrene ion gives rise to a kinetic shift in the observation of the product ions on our experimental timescale of approximately 3 eV.

Figure 6. iPEPICO breakdown curves for ionized 1-hydroxypyrene. Solid lines are the RRKM fit to the experimental data (markers).

Figure 7. Time-of-flight distributions as a function of photon energy for ionized 1-hydroxypyrene. Gaussian peaks at 16.9 and 17.6 μs correspond to impurities from a previously-introduced sample of nitropyrene. Both CO- and HCO-loss components were needed to fit the experimental data between 16.4 and 17.2 μs , ignoring the impurity peaks.

The main difference between the theoretical reaction pathways and the iPEPICO-derived data are the reaction energies. The highest energy point in the CO-loss mechanisms was calculated (CCSD/6-31G(d)//B3-LYP/6-31G(d) level of theory) to be at an energy of 3.58 eV relative to the molecular ion, and that for HCO-loss was approximately 0.7 eV higher at 4.25 eV, compared to the IPEPICO-derived values of 2.91 ± 0.05 eV and 3.92 ± 0.05 eV, respectively, indicating that this level of theory is overestimating the activation energies.

CONCLUSION

Hydroxy-substituted PAH ions dissociate primarily by CO- and HCO-loss in CID mass spectrometry experiments, with the relative importance of H-loss decreasing with increasing molecular size. Calculated reaction pathways for the competing CO- and HCO-forming reactions in 1-hydroxypyrene ions provided the rational for the difference in $\Delta^\ddagger S$ for the two reactions required to qualitatively understand the CID breakdown curves. An iPEPICO determination of the CO- and HCO-loss reaction energies, 2.91 ± 0.05 eV and 3.92 ± 0.05 eV, respectively, were lower than those predicted by CCSD/6-31G(d)//B3-LYP/6-31G(d) level calculations, but the $\Delta^\ddagger S_{600K}$ values derived were consistent with the observed change in competition between the two channels with increasing energy. Thus, photo-processing of larger hydroxy-substituted PAH ions in the ISM should yield both CO and HCO small neutral molecules, with a preference for HCO at high photon energies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: . The complete citation for reference 14 and Figure S1, the calculated reaction pathways for the loss of HCO and CO from ionized 1-naphthol (PDF). Vibrational frequencies and RRKM rate constants used to model the iPEPICO data can be found in supporting information, Table S1 (XLXS).

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Notes

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REFERENCES

- (1) Chan, K.-W. R.; T. L.; Onaka, T.; Mizutani, M.; Okumura, K.; Yamamura, I.; Tanabé, T.; Shibai, H.; T. Nakagawa; Okuda, H. Unidentified infrared emission bands in the diffuse interstellar medium. *ApJ* **2001**, 546, 273-278.
- (2) *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.
- (3) Irvine, W. M. Extraterrestrial organic matter: A review *Origins of life and evolution of the biosphere* **1998**, 28, 365-383.
- (4) Sadjadi, S.; Zhang, Y.; Kwok, S. On the origin of the 11.3 micron unidentified infrared emission feature *Ap. J.* **2015**, 807, 95 (11p).
- (5) Gudipati, M. S.; Yang, R. In-situ probing of radiation-induced processing of organics in astrophysical ice analogs—novel laser desorption laser ionization time-of-flight mass spectroscopic studies *Ap. J. Lett.* **2012**, 756, L24 (25pp).
- (6) Cook, A. M.; Ricca, A.; Mattioda, A. L.; Bouwman, J.; Roser, J.; Linnartz, H.; Bregman, J.; Allamandola, L. J. Photochemistry of polycyclic aromatic hydrocarbons in cosmic water ice: The role of PAH ionization and concentration *Ap. J.* **2015**, 799, 14 (20 pp).
- (7) Hardegree-Ullman, E. E.; Gudipati, M. S.; Boogert, A. C. A.; Lignell, H.; Allamandola, L. J.; Stapelfeldt, K. R.; Werner, M. Laboratory determination of the infrared band strengths of pyrene frozen in water ice: Implications for the composition of interstellar ices *arXiv.org, e-Print Archive, Astrophysics* **2014**, 1-28.
- (8) Vaikkinen, A.; Kaupila, T. J.; Kostianen, R. Charge exchange reaction in dopant-assisted atmospheric pressure chemical ionization and atmospheric pressure photoionization *J. Am. Soc. Mass Spectrom.* **2016**, 27 1291-1300.
- (9) Bodi, A.; Hemberger, P.; Gerber, T.; Sztáray, B. A new double imaging velocity focusing coincidence experiment: i²PEPICO. *Rev. Sci. Instrum.* **2012**, 83, 083105.
- (10) Bodi, A.; Sztaray, B.; Baer, T.; Johnson, M.; Gerber, T. Data acquisition schemes for continuous two-particle time-of-flight coincidence experiments *Rev. Sci. Instrum.* **2007**, 78, 084102.
- (11) Sztáray, B.; Bodi, A.; Baer, T. Modeling unimolecular reactions in photoelectron photoion coincidence experiments *J. Mass Spectrom.* **2010**, 45, 1233-1245.
- (12) Hemberger, P.; Custodis, V. B. F.; Bodi, A.; Gerber, T.; Bokhoven, J. A. v. Understanding the mechanism of catalytic fast pyrolysis by unveiling reactive intermediates in heterogeneous catalysis *Nat. Commun.* **2017**, 8, 15946.
- (13) Sztáray, B.; Baer, T. Suppression of hot electrons in threshold photoelectron photoion coincidence spectroscopy using velocity focusing optics *Rev. Sci. Instr.* **2003**, 74, 3763-3768.
- (14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H. *et. al.*, Gaussian 16 rev. B.01, Wallingford, CT, 2016.
- (15) Baer, T.; Mayer, P. M. Statistical Rice-Ramsperger-Kassel-Marcus quasiequilibrium theory calculations in mass spectrometry *J. Am. Soc. Mass Spectrom.* **1997**, 8, 103-115.

- (16) Baer, T.; Hase, W. L., *Unimolecular reaction dynamics, theory and experiments*. Oxford University Press: New York, 1996.
- (17) Beyer, T.; Swinehart, D. R. Number of multiply-restricted partitions [a1] (algorithm 448) *ACM Commun.* **1973**, 16, 379.
- (18) Burner, J.; West, B. J.; Mayer, P. M. What will photo-processing of large, ionized amino-substituted polycyclic aromatic hydrocarbons produce in the interstellar medium? *J. Phys. Chem. A* **2019**, 123, 5027-5034.
- (19) West, B.; Lowe, B.; Mayer, P. M. Unimolecular dissociation of 1-methylpyrene cations: Why are 1-methylenepyrene cations formed and not a tropylium-containing ion? *J. Phys. Chem. A* **2018**, 122, 4730-4735.
- (20) West, B. J.; Lesniak, L.; Mayer, P. M. Why do large PAHs not lose C₂H₂? *J. Phys. Chem A* **2019**, 123, 3569-3574.
- (21) Baer, T.; Brand, W. A.; Bunn, T. L.; Butler, J. J. Isomerization of internal energy selected ions *Faraday Discuss. Chem. Soc.* **1983**, 75, 45-55.

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