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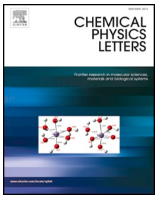

Research paper

Electron-induced proton transfer (EIPT) in 2-hydroxypyridine/2-pyridone tautomeric dimer anions: A photoelectron spectroscopic and density functional theory study

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HIGHLIGHTS

- Photoelectron spectra (PES) of 2-hydroxypyridine/2-pyridone dimer anions were taken.
- The PES showed a vertical detachment energy (VDE) of 1.21 ± 0.05 eV.
- Density functional theory (DFT) results closely matched the measured VDE.
- DFT showed that electron-induced proton transfer (EIPT) had occurred.
- All combinations of neutral dimers showed EIPT between the neutral and its anion.

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ABSTRACT

Anion photoelectron spectroscopy and density functional theory computations were conducted on the 2-hydroxypyridine/2-pyridone tautomeric dimer anion system. Their experimentally-measured, composite vertical detachment energy (VDE) of 1.21 ± 0.05 eV compares well with their theoretically-determined VDE values of 1.15 eV and 1.20 eV, supporting our conclusion that intermolecular electron-induced proton transfer (EIPT) has taken place in these dimer anions.

1. Introduction

Electron-induced proton transfer (EIPT) is a well-known process in radiation biology, where its occurrence is facilitated by the presence of myriad secondary electrons, generated by ionizing radiation [1,2,3,4]. More recently, the electron-induced proton transfer mechanism has also been studied in gas-phase systems, most typically in anionic dimers [5,6,7,8,9].

The 2-hydroxpyridine and 2-pyridone molecules are tautomers. Both their homogeneous and heterogeneous dimers each form two hydrogen bonds. Since these dimers exhibit structural similarities to DNA base pairs, they have been studied as models for proton transfer among the hydrogen bonds in base pairs. In particular, ultraviolet and infrared spectroscopic studies of neutral 2-hydroxypyridine/2-pyridone dimers found evidence for double proton transfer tautomerization in the dimers' excited states, although neither single or double proton transfer was observed in their ground states [10]. Additional studies on both the neutral 2-hydroxypyridine and 2-pyridone molecules and their cations utilized NMR [11], microwave [12], zero electron kinetic energy (ZEKE) [13] and time-resolved spectroscopies [14]. Several computational studies have also been conducted [15,16,17,18].

Here, we present a negative ion photoelectron spectroscopic study of the 2-hydroypyridine/2-pyridone dimer anions. Their vertical detachment energy (VDE) was determined from their composite anion photoelectron spectrum. Geometry and energy calculations on 2-hydroxypyridine/2-pyridone homogeneous and heterogeneous, anionic and neutral dimers were conducted using density functional theory. Agreement between our measured and calculated VDE values of 1.21 ± 0.05 eV and 1.15/1.20 eV, respectively, supported our conclusion that electron-induced proton transfer had occurred.

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2. Experimental methods

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency beam of photons and energy-analyzing the resultant photodetached electrons. This technique is based on the energy conserving relationship, $h\nu$ = EKE + EBE, where EKE is electron kinetic energy, EBE is electron binding energy, and $h\nu$ is the photon energy. In the present experiment, negative ions were formed in a supersonic expansion nozzle-ion source. There, a 2-hydroxypyridine/2-pyridone sample was placed in a stagnation chamber, heated to 40–50 °C, and co-expanded with 2–3 atm of argon gas through a 23 μm orifice into a 10^{-4} torr vacuum. A hot, negatively biased thoriated iridium filament injected low energy electrons, in the presence of a weak magnetic field, into the resulting gas expansion, producing negative ions. These anions were then extracted, collimated, and transferred into the flight tube of a 90∘ magnetic sector mass spectrometer. The mass-selected parent dimer anions of interest were then crossed with the intracavity laser beam of an argon ion laser, operating at 2.54 eV/photon (488 nm). The resulting photodetached electrons were then energy analyzed in a hemispherical electron energy analyzer with a typical resolution of 25 meV. Photoelectron spectra of the 2-hydroxypyridine/2-pyridone dimer anions were calibrated against the well-known spectrum of O^- [19]. A detailed description of our apparatus has been given elsewhere [20].

3. Computational methods

Density functional theory (DFT) calculations of the neutral and anionic, homogeneous and heterogeneous, 2-hydroxypyridine/2-pyridone dimer anions were performed by applying the wb97xd [21] functional using the Gaussian09 software package [22]. The geometries of dimer anions and their corresponding neutral dimers were fully optimized using the 6-31 + G (p,d) basis set [23]. The electronic energies were then improved by single–point calculations using the 6-311+ + G(3d,3pd) basis set at optimized geometries [24]. The highest occupied molecular orbital (HOMO) of the relaxed anion was formulated using GaussView.

4. Results and discussion

Both homogeneous and heterogeneous, 2-hydroxypyridine/2-pyridone dimer anions exist together is the beam. Their composite anion photoelectron spectrum is presented in Fig. 1. The EBE of the intensity maximum in its photoelectron spectrum is 1.21 ± 0.05 eV. This is its VDE value. The anion photoelectron spectrum consists of a broad, unresolved band, consistent with the photodetachment of a stable valence anion, whose geometric structure differs significantly from that of its neutral counterpart. Our previous studies of base pair anions, which had undergone EIPT also showed similarly broad spectra with VDE values in the same energy range [5,6,7]. Fig. 2 presents a low electron count photoelectron spectrum of the singly-hydrated, mixed 2-hydroxypyridine/2-pyridone dimer anion. Its VDE value is ~1.4 ± 0.1 eV. This is shifted relative to its un-hydrated counterpart by ~0.2 eV. This energy is equivalent to the energy difference between the mixed 2-hydroxypyridine/2-pyridone dimer anion - water molecule dissociation energy and the neutral mixed 2-hydroxypyridine/2-pyridone dimer - water molecule dissociation energy, where the former contribution likely dominates. Since anion-water interaction energies are usually two or more times this value, 0.2 eV suggests that the negative charge seen by the water molecule is significantly delocalized.

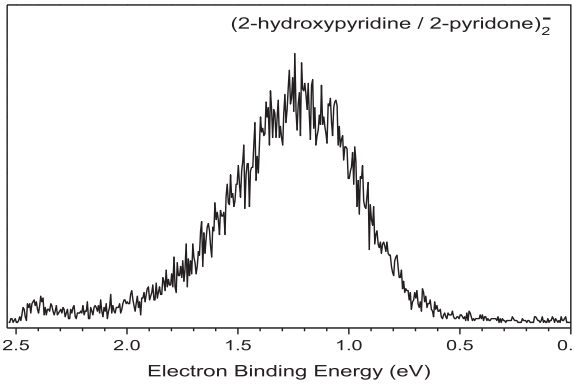

Fig. 1. The negative ion photoelectron spectrum of the (2-hydroxypyridine/2-pyridone)$_2^-$ dimer anion recorded using 2.540 eV photons.

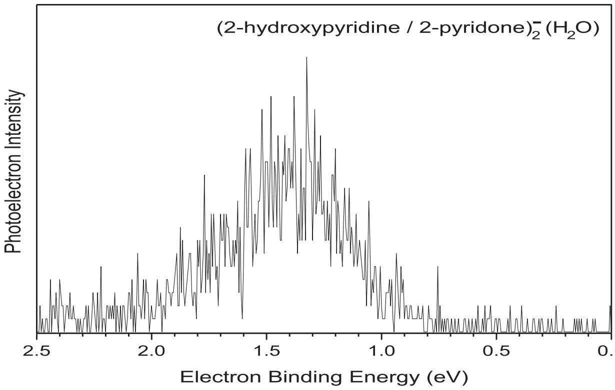

Fig. 2. The negative ion photoelectron spectrum of the (2-hydroxypyridine/2-pyridone)$_2^-$(H_2O) hydrated dimer anion recorded using 2.540 eV photons.

Since 2-hydroxypyridine and 2-pyridone are tautomers, we carried out DFT calculations to determine the optimal geometries of its three possible neutral tautomeric dimers, i.e., (2-hydroxypyridine)$_2$, (2-pyridone)$_2$, and (2-hydroxypyridine)(2-pyridone), and in each case of their corresponding dimer anions, that had been formed by EIPT. Fig. 3 presents these six structures, with the neutral dimers (in the upper row) labelled as 1n, 2n, and 3n and with their respective EIPT-formed dimer anions (in the lower row) labelled as 1a, 1a, and 2a. (Note that the first two of these dimer anion structures are identical. Thus, they are both labelled as 1a and 1a.)

The calculated absolute energies, O—H bond lengths, the experimental VDE values, and the calculated VDE values are tabulated in Table 1. Geometry optimizations for all three neutral dimers indicate that none of them undergo proton transfer, in agreement with earlier literature results [10]. Geometry optimizations for their three corresponding dimer anions, however, clearly show that they all have undergone proton transfer. These single proton transfers were induced by the addition of an excess electron, i.e., EIPT has occurred in each case. The newly formed O—H bonds in 1a and 2a, i.e., from 2n + $e^- \rightarrow$ 1a and from 3n + $e^- \rightarrow$ 2a, are 1.174 Å and 1.178 Å, respectively. These values are comparable at typical O—H bond lengths, e.g., 0.96 Å, implying that the protons have been successfully transferred. The calculated VDE values of 1a and 2a were found to be quite similar, 1.15 eV and 1.20 eV, respectively.

In intermolecular EIPT, one molecule acts as a base, while the other plays the role of the Bronsted acid. Once the excess electron attaches to the base, the resulting momentary anion becomes able to pull a proton from the acid to protonate itself, producing a neutral base hydride radical moiety and a deprotonated acid moiety. Fig. 4 shows the HOMO of a relaxed 1a anion, showing that the excess electron is delocalized on the $\pi*$ anti-bonding orbital of the neutral base hydride radical moiety. This radical then interacts with its deprotonated acid moiety through hydrogen bonds. Also consistent with this picture, the lowest EBE electron to be photodetached comes from the neutral base hydride radical moiety, not from the deprotonated acid moiety. Together, the anion photoelectron spectrum and our theoretical results show that

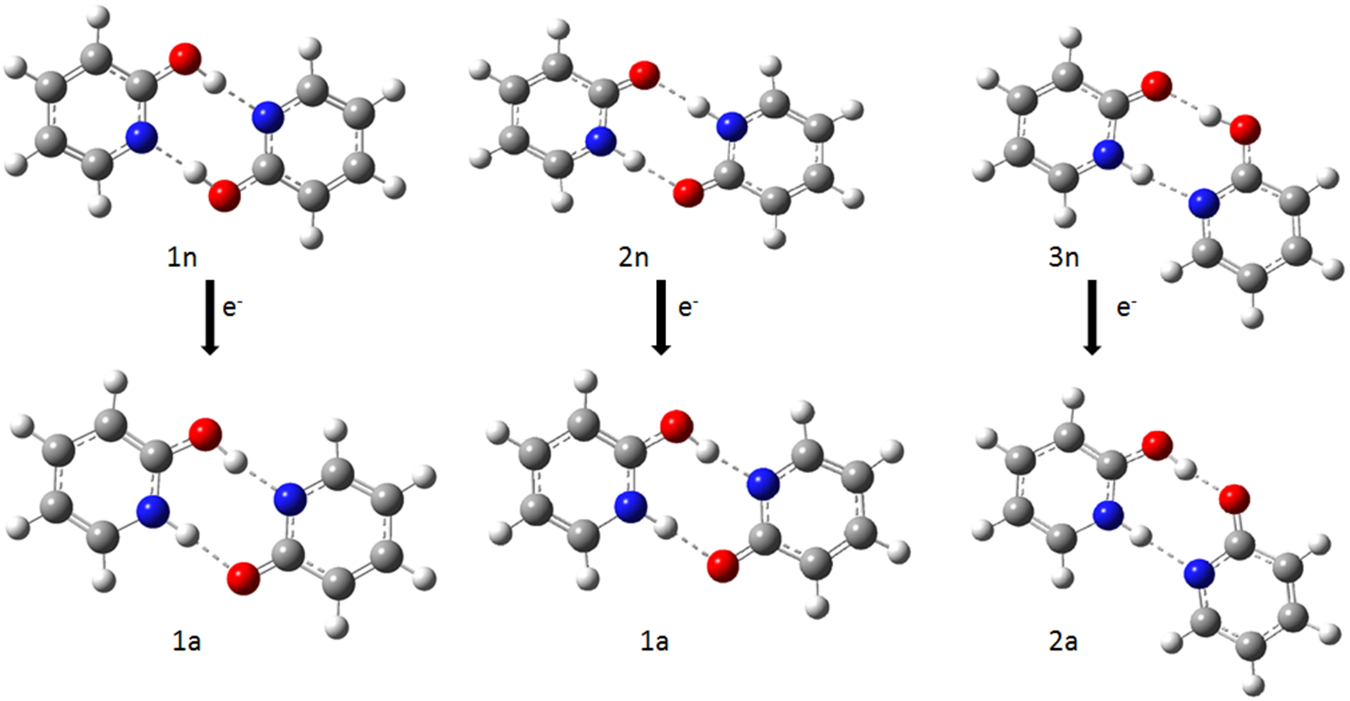

Fig. 3. Electron-induced proton transfer in three 2-hydroxypyridine/2-pyridone dimer tautomers: the neutral 2-hydroxypyridine homogeneous dimer, the neutral 2-pyridone homogeneous dimer and the neutral 2-pyridone/2-hydroxypyridine heterogeneous dimer are noted as 1n, 2n, 3n respectively. Their corresponding anions, formed by EIPT, are noted as 1a and 2a accordingly.

Table 1
Calculated and experimental vertical detachment energies (VDE), absolute energies, and newly formed O—H bond lengths pertaining to the neutral dimers and their dimer anions.

	Absolute Energy (Hartree)	Calculated VDE (eV)	Experimental VDE (eV)	O—H Bond Length (Å)
1n	−647.0358918			
1a	−647.0782765	1.15	1.21	
2n	−647.0358923			
1a	−647.0782765	1.15		1.174
3n	−647.0335289			
2a	−647.0777499	1.20		1.178

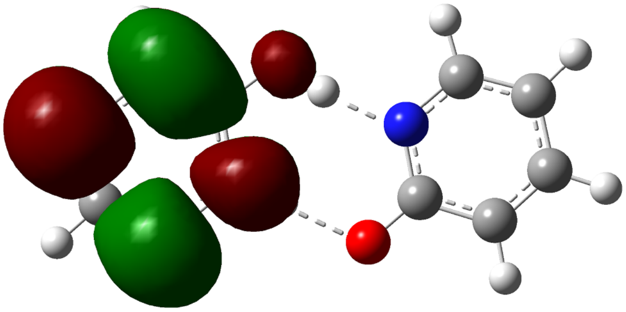

Fig. 4. The highest occupied molecular orbital (HOMO) of the ground state of the (2-hydroxypyridine/2-pyridone)$_2^-$ dimer anion at the wb97xd/6-31+G (p,d) level of theory.

electron-induced proton transfer (EIPT) has occurred within these dimer anions.

5. Conclusion

Experimental and theoretical results complement one another and support the conclusion that in the 2-hydroxypyridine/2-pyridone system electron-induced proton transfer (EIPT) occurs in both possible dimer anion combinations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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