Photoelectron Spectroscopy of Anilinide and Acidity of Aniline

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ABSTRACT: The photoelectron spectrum of the anilinide ion has been measured. The spectrum exhibits a vibrational progression of the CCC in-plane bending mode of the anilino radical in its electronic ground state. The observed fundamental frequency is 524 ± 10 cm\(^{-1}\). The electron affinity (EA) of the radical is determined to be 1.607 ± 0.004 eV. The EA value is combined with the N\(^{-}\)H bond dissociation energy of aniline in a negative ion thermochemical cycle to derive the deprotonation enthalpy of aniline at 0 K; \(\Delta_{\text{acid}} H_0(\text{PhHN}^{-}\text{H}) = 1535.4 \pm 0.7 \text{ kJ mol}^{-1}\). Temperature corrections are made to obtain the corresponding value at 298 K and the gas-phase acidity; \(\Delta_{\text{acid}} H_{298}(\text{PhHN}^{-}\text{H}) = 1540.8 \pm 1.0 \text{ kJ mol}^{-1}\) and \(\Delta_{\text{acid}} G_{298}(\text{PhHN}^{-}\text{H}) = 1509.2 \pm 1.5 \text{ kJ mol}^{-1}\), respectively. The compatibility of this value in the acidity scale that is currently available is examined by utilizing the acidity of acetaldehyde as a reference.

1. INTRODUCTION

Aromatic compounds constitute a significant portion of liquid fuels in general. Toluene is a representative and its pyrolysis and high temperature oxidation have long been investigated to better understand the combustion process.\(^1\)\(^-\)\(^3\) The primary initial reaction in the process yields the benzyl radical (Scheme 1).\(^2\) This resonance-stabilized radical has been a subject of a large number of spectroscopic and thermochemical studies,\(^4\)\(^-\)\(^10\) revealing many aspects of its molecular properties. The phenyl radical is also generated from toluene in the combustion environment.\(^2\) Ensuing oxidation mainly converts phenyl into the phenoxyl radical (Scheme 1).\(^1\)\(^,\)\(^11\) Analogous to benzyl, a plethora of spectroscopic studies of phenoxyl have been reported in the literature.\(^4\)\(^,\)\(^5\)\(^,\)\(^10\)\(^-\)\(^12\)\(^-\)\(^15\)

Besides these radicals relevant to combustion, another isoelectronic species, the anilino radical (Scheme 1), has also been studied to a moderate extent.\(^4\)\(^,\)\(^8\)\(^-\)\(^10\)\(^-\)\(^18\) Recently, Ashfold and co-workers conducted a H Rydberg atom photofragment translational spectroscopic study of aniline.\(^18\) The kinetic energy release spectra recorded following an electronic transition of aniline expose some vibrational level structure of the anilino radical. The analysis of the spectra afforded the N\(^{-}\)H bond dissociation energy (BDE) of aniline, \(D_0(\text{PhHN}^{-}\text{H})\).

The photoelectron spectrum of the anilinide ion has been measured in the present study to determine the EA value of the anilino radical and, in turn, the acidity of aniline through eq 1. This valuable thermochemical quantity can be utilized to deduce another important thermochemical property, the gas-phase acidity of aniline, from the following negative ion thermochemical cycle,\(^19\)

\[
\Delta_{\text{acid}} H_0(\text{PhHN}^{-}\text{H}) = D_0(\text{PhHN}^{-}\text{H}) - \text{EA(PhNH}^+\text{)} + \text{IE(H}^+\text{)}
\]

(1)

Here, \(\Delta_{\text{acid}} H_0(\text{PhHN}^{-}\text{H})\) is the N\(^{-}\)H deprotonation enthalpy of aniline at 0 K, which is equivalent to the gas-phase acidity at 0 K, \(\text{EA(PhNH}^+\text{)}\) is the electron affinity of the anilino radical, and \(\text{IE(H}^+\text{)}\) is the ionization energy of the H atom, which is very accurately known.\(^20\) Aniline is located in a region of the acidity scale where a reference acid with an accurate acidity is desired to anchor the scale in the vicinity.\(^21\)\(^-\)\(^26\)

The photoelectron spectrum of the anilinide ion has been measured in the present study to determine the EA value of the anilino radical and, in turn, the acidity of aniline through eq 1. The acidity of aniline so obtained is incorporated into the existent acidity scale to assess its utility. The results of recent HEAT calculations by Tabor et al.\(^27\) are invoked for critical evaluation of the thermochemical scale; specifically the relative acidity of aniline against acetaldehyde. Also, the analysis of the...
photoelectron spectrum gives information about the vibrational level structure of the anilino radical, which is compared to a previous resonance Raman study by Tripathi.\textsuperscript{17}

2. EXPERIMENTAL AND THEORETICAL METHODS

The negative ion photoelectron spectrometer has been described in detail elsewhere.\textsuperscript{25,29} Negative ions are formed in a flowing afterglow ion source. A microwave discharge containing trace amounts of \( \text{O}_2 \) in helium buffer gas (\( \sim \)0.4 Torr) generates the atomic oxygen radical anions (\( \text{O}^- \)). Methane is added downstream and reacts with \( \text{O}^- \) to form the hydroxide ion (\( \text{HO}^- \)). The \( \text{HO}^- \) ion subsequently reacts with aniline (\( \geq 98.5\% \), Sigma-Aldrich) added further downstream to generate the anilinide ion. Collisions with He buffer gas thermalize the product ions to \( \sim \)300 K. The flow tube can also be cooled with a flow of liquid nitrogen to reduce the ion temperature down to below 200 K. The negative ions are extracted into a differentially pumped region and are accelerated to 735 eV before entering a Wien velocity filter with a mass resolution \( m/\Delta m \sim 60 \). The mass-selected anilinide ion beam (typically 100 pA) is decelerated to 35 eV and focused into the interaction region. Here, the \( \sim \)1 W output from a single-mode continuous-wave argon ion laser operating at 363.8 nm (3.408 eV) is amplified to 35 eV and focused into the interaction region. The energy resolution of the analyzer is 8–10 meV. The electron binding energy is the difference between the electron kinetic energy and the photon energy and the electron kinetic energy range. A rotatable half-wave plate positioned outside the buildup cavity is adjusted to control the polarization of the laser beam such that it makes the magic angle relative to the photoelectron collection axis. Thus, the photoelectron count rates at all kinetic energies are uniformly proportional to the corresponding photodetachment cross sections.

Electronic structure calculations were performed with the Gaussian 03 software package.\textsuperscript{32} A variant of density functional theory (DFT), B3LYP,\textsuperscript{33} and the 6-311++G(\( \text{d,p} \)) basis set\textsuperscript{34} were employed. The optimized geometries and harmonic vibrational frequencies of relevant species are provided in the Supporting Information. The Franck–Condon factors were calculated using the PESCAL program\textsuperscript{35} under the harmonic assumption.

3. RESULTS AND DISCUSSION

3.1. Photoelectron Spectrum of Anilinide. The photoelectron spectrum of anilinide is displayed in Figure 1a. DFT calculations aid in spectral analysis. The calculations find potential energy minima at planar geometries for both the anilinide ion and the anilino radical (see the Supporting Information). The calculated EA of the radical is 1.595 eV, which is close to the eBE of the most intense peak (peak A). Figure 1b shows the simulation of the spectrum, which is based on the DFT geometries and the harmonic vibrational analysis (see the Supporting Information). The simulation assumes an ion temperature of 300 K and a full width at half-maximum of 15 meV. The eBE for the simulated vibrational origin transition is set to that of peak A. The good quality of the simulation is evident. Thus, the EA of the anilino radical is determined to be 1.607 \( \pm \) 0.004 eV. The present EA value is a large improvement over the previous one estimated from threshold photodetachment measurements.\textsuperscript{6} The simulation also establishes that the observed vibrational progression represents the CCC in-plane bending mode of the anilinide radical (\( \nu_{22} \)) with a fundamental frequency of 524 \( \pm \) 10 cm\(^{-1} \). Measurements with lower ion temperatures (\( \leq 200 \) K) confirm that peak a is a hot band due to the corresponding mode of anilinide with a fundamental frequency of 517 \( \pm \) 10 cm\(^{-1} \). The observed peak positions are listed in Table 1.

Figure 2 illustrates the highest-occupied molecular orbital (HOMO) of anilinide. This \( \pi \) orbital has bonding interactions for two pairs of CC bonds. Photodetachment from the HOMO diminishes the favorable interactions, resulting in geometry shift with respect to the in-plane CCC angles (see the Supporting Information). This shift accounts for the appearance of the \( \nu_{22} \) vibrational progression in the spectrum. The \( \nu_{22} \) mode corresponds to the Wilson 6a mode for benzene (CCC in-plane bending)\textsuperscript{36} and its atomic displacements are depicted in Figure 2. It is relevant to compare the spectrum of anilinide with those of the isoelectronic ions; the benzyl anion\textsuperscript{10} and the...
Andrews measured 520 cm⁻¹. The fundamental level of the 6a mode of the phenoxyl radical was found for the radical in the gas phase by Fukushima and colleagues using velocity-map imaging spectroscopic study. Tripathi and co-workers measured by Neumark and co-workers in a slow photoelectron spectra. The corresponding fundamental frequencies are also remarkably similar. The HOMOs of the three ions resemble each others, and the same Wilson 6a mode is active in these radicals, however, the NH₂ inversion modes of aniline, however, the NH₂ inversion modes are not amenable to the harmonic treatment. A one-dimensional model Hamiltonian is constructed for each of the two modes, and the corresponding partition function is obtained from the eigenvalues of the Hamiltonian. Details of such analysis are provided in the Supporting Information. It has been derived that ΔacidH₂98(PhHN−H) = 1540.8 ± 1.0 kJ mol⁻¹ and ΔacidG₂98(PhHN−H) = 1509.2 ± 1.5 kJ mol⁻¹. These thermochemical data are summarized in Table 2.

<table>
<thead>
<tr>
<th>peak</th>
<th>peak position (cm⁻¹)</th>
<th>assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>−517 ± 10</td>
<td>22槿</td>
</tr>
<tr>
<td>A</td>
<td>0</td>
<td>0槿</td>
</tr>
<tr>
<td>B</td>
<td>524 ± 10</td>
<td>22槿</td>
</tr>
<tr>
<td>C</td>
<td>1047 ± 15</td>
<td>22槿</td>
</tr>
<tr>
<td>D</td>
<td>1549 ± 20</td>
<td>22槿</td>
</tr>
</tbody>
</table>

“The peak labels are shown in Figure 1. The peak positions are given relative to that for the vibrational origin transition. The ν₂₁ mode represents CCC in-plane bending motion (Wilson 6a mode; see Figure 2).”

**Figure 2.** Atomic displacements of the ν₂₁ mode of the anilino radical and a pictorial representation of the HOMO of the anilinium ion.

The profiles of these photoelectron spectra are remarkably similar. The HOMOs of the three ions resemble each others, and the same Wilson 6a mode is active in these spectra. The corresponding fundamental frequencies are also comparable: 514 ± 15, 524 ± 10, and 519 cm⁻¹, respectively, for the benzyl, anilino, and phenoxyl radicals according to the photoelectron spectroscopic measurements. Miller and Andrews measured 520 cm⁻¹ for the 6a mode of the benzyl radical in a low-temperature Ar matrix. The same frequency was found for the radical in the gas phase by Fukushima and Obi. The fundamental level of the 6a mode of the phenoxyl radical was detected at 520 cm⁻¹ in a low-temperature Ar matrix by Radziszewski and co-workers. This frequency is very close to the corresponding one in the gas phase, 519 cm⁻¹, measured by Neumark and co-workers in a slow photoelectron velocity-map imaging spectroscopic study. Tripathi and Schuler observed 533 and 528 cm⁻¹ for the 6a mode of the anilino and phenoxyl radicals, respectively, in aqueous solution.

In contrast to this similarity of the vibrational structure, the EAs of the three isoelectronic radicals are quite different, and they are correlated with the electronegativities of the substituents: 0.912 ± 0.006, 1.607 ± 0.004, and 2.2538 ± 0.0008 eV, respectively, for benzyl, anilino, and phenoxyl. The EA of the anilino radical, 1.607 ± 0.004 eV (1312.0494 kJ mol⁻¹) was recently measured by Neumark and co-workers; reference 18. The EA(H) = 1.5 kJ mol⁻¹.

**Table 2. Summary of Thermochemical Values**

<table>
<thead>
<tr>
<th>Aniline System</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₀(PhHN−H)</td>
<td>378.4 ± 0.5 kJ mol⁻¹</td>
</tr>
<tr>
<td>EA(PhNH₃)</td>
<td>1.607 ± 0.004 eV</td>
</tr>
<tr>
<td>ΔacidH₂98(PhHN−H)</td>
<td>1535.4 ± 0.7 kJ mol⁻¹</td>
</tr>
<tr>
<td>ΔacidH₂98(PhHN−H)</td>
<td>1540.8 ± 1.0 kJ mol⁻¹</td>
</tr>
<tr>
<td>ΔacidG₂98(PhHN−H)</td>
<td>1509.2 ± 1.5 kJ mol⁻¹</td>
</tr>
<tr>
<td>Acetaldehyde System</td>
<td></td>
</tr>
<tr>
<td>D₀(OHCH₂C−H)</td>
<td>394.6 ± 1.6 kJ mol⁻¹</td>
</tr>
<tr>
<td>EA(OHCH₂C−H)</td>
<td>1.8250 ± 0.0012 eV</td>
</tr>
<tr>
<td>ΔacidH₂98(OHCH₂C−H)</td>
<td>1530.6 ± 1.6 kJ mol⁻¹</td>
</tr>
<tr>
<td>ΔacidH₂98(OHCH₂C−H)</td>
<td>1535.7 ± 1.6 kJ mol⁻¹</td>
</tr>
<tr>
<td>ΔacidG₂98(OHCH₂C−H)</td>
<td>1506.0 ± 1.7 kJ mol⁻¹</td>
</tr>
</tbody>
</table>

“Reference 18. Experimentally determined in the present work. Evaluated in the present work. Evaluated with data from refs 27, 44, and 45. Reference 42.”

**3.3. Aniline in the Acidity Scale**

This determination of the aniline acidity is deemed valuable in establishing an accurate gas-phase acidity scale. In a classic paper by McIver and co-workers, relative acidities of aniline were reported in reference to a number of molecules. These relative acidities can be used to examine the consistency of the acidity scale. The most useful reference acid in this context appears to be acetaldehyde. The proton transfer reaction,

\[ \text{PhNH}^- + \text{OHCH}_3 \rightleftharpoons \text{PhNH}_2 + \text{OHCH}_2^- \]

has ΔG₂98(forward reaction 2) = −0.4 kJ mol⁻¹, according to the equilibrium measurements. When this free energy difference is combined with the acidity of aniline, it is found ΔacidG₂98(OHCH₂C−H) = 1508.8 ± 1.5 kJ mol⁻¹. The question at this point is how this acidity of acetaldehyde compares with those determined through independent procedures.

Analogous to eq 1, the gas-phase acidity of acetaldehyde can be derived through a negative ion thermochemical cycle,

\[ \Delta_{\text{acid}}H_0(\text{OHCH}_2C−H) = D_0(\text{OHCH}_2C−H) - \text{EA(OHCH}_2^\bullet) + \text{IE(H}^\bullet) \]

(3)

The EA of the vinoxy radical has recently been measured by Neumark and co-workers; reference 18. EA(OHCH₂C−H) = 1.8250 ± 0.0012 eV. The C−H BDE of acetaldehyde can be derived from the following equation,

\[ D_0(\text{OHCH}_2C−H) = \Delta_H(\text{OHCH}_2^\bullet) + \Delta_H(\text{H}^\bullet) - \Delta_H(\text{OHCH}_3) \]

(4)
On the right-hand side of eq 4 is the standard enthalpy of formation of the vinoxy radical. Recently, Tabor et al. determined $\Delta H_0^\circ$(OHCH$_2$C•) = 23.4 ± 1.5 kJ mol$^{-1}$ with an ab initio model chemistry technique, known as HEAT.$^{27,43}$ According to the active thermochemical tables (ATcT),$^{44,45}$ $\Delta H_0^\circ$(H$^+$) = 216.034 kJ mol$^{-1}$ and $\Delta H_0^\circ$(OHCH$_3$) = −155.2 ± 0.5 kJ mol$^{-1}$. Substituting these values into eq 4, one obtains $D_2$(OHCH$_2$C•) = 394.6 ± 1.6 kJ mol$^{-1}$. In turn, eq 3 gives $\Delta$acid$H_2$(OHCH$_2$C•−) = 1530.6 ± 1.6 kJ mol$^{-1}$. Temperature corrections to the acidity are made under the rigid-rotor-harmonic approximation except for the methyl torsion mode.$^{46}$

Readers are referred to the Supporting Information for the details of the temperature corrections. It is found that $\Delta$acid$H_2$9298(OHCH$_2$C•−) = 1535.7 ± 1.6 kJ mol$^{-1}$ and $\Delta$acid$G_2$9298(OHCH$_2$C•) = 1506.0 ± 1.7 kJ mol$^{-1}$. The uncertainty of this acidity value has a small overlap with that determined with high-pressure mass spectrometric experimentally.$^{27}$ It is also noteworthy that the gas-phase acidity of acetaldehyde when the results of a recent HEAT study$^{27}$ of the vinoxy radical are utilized. It has been found that $\Delta$acid$H_2$(OHCH$_2$C•−) = 1530.6 ± 1.6 kJ mol$^{-1}$, $\Delta$acid$H_2$(OHCH$_2$C•) = 1535.7 ± 1.6 kJ mol$^{-1}$, and $\Delta$acid$G_2$(OHCH$_2$C•−) = 1506.0 ± 1.7 kJ mol$^{-1}$. Establishing these acidity values helps ongoing efforts to construct accurate acidity ladder scales.$^{25,26,53}$

## ASSOCIATED CONTENT

### Supporting Information

Results of quantum chemical calculations and details of thermodynamic analysis (including tables of vibrational frequencies and molecular constants and a structure with optimized geometries). This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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