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1. Introduction

Oxazole is the parent molecule for a large class of heterocyclic aromatic compounds. The electronic properties of oxazole have been studied *via* a variety of methods,^{1–7} but these investigations focused primarily on the closed-shell neutral molecule and its corresponding cation. The wide-ranging applications of oxazole, such as in organic synthesis and pharmaceuticals, spark interest in the anionic and reactive-intermediate forms of this important molecule.

In this work, we interrogate the oxazolyl radical, ${}^{\circ}C_{3}H_{2}NO$, which is formed *via* the cleavage of a C–H bond in oxazole. Like other heterocyclic intermediates, this radical is a highly reactive species involved in a variety of chemical processes. Due to this reactive nature, the oxazolyl radical is difficult to isolate. We access this radical *via* photodetachment of the closed-shell oxazolide anion, $C_{3}H_{2}NO^{-}$, generated by deprotonation of oxazole.

As illustrated in Fig. 1, the H/H⁺ elimination from oxazole can occur at three non-equivalent positions (C2, C4, or C5). Theoretical calculations are not conclusive as to which anion isomer is most stable, but collision-induced dissociation studies by Adams *et al.* have shown that deprotonation occurs preferentially at the C2 position.⁸ In the present work, we demonstrate selective deprotonation of oxazole exclusively at the C2 position. Specifically, the synthesis of deuterated 2-D-oxazole is reported, followed by mass-spectrometry measurements which demonstrate generation of the anion resulting from deprotonation (de-deuteration) at the C2 position. We then use photoelectron imaging spectroscopy of the C2-oxazolide anion to examine the electron affinity (EA),

Selective deprotonation of oxazole and photoelectron imaging of the oxazolide anion

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A photoelectron imaging study of the oxazolide anion obtained by selective deprotonation of oxazole at the C2 position is reported. The photodetachment transitions observed at 355, 392, and 532 nm are assigned to the ground state of the neutral oxazolyl σ radical. A Franck–Condon analysis of this transition aids in the first determination of the adiabatic electron affinity of oxazolyl, EA = 2.21 \pm 0.02 eV. A vibrational progression with a frequency of 890 \pm 80 cm⁻¹ is observed, corresponding to an in-plane ring distortion mode. The photoelectron angular distributions are analyzed using the mixed s–p model, shedding light on the hybrid character of the anion HOMO.

thermodynamic stability, and vibrational structure of the C2-oxazolyl radical. By examining the photoelectron angular distributions (PAD) we gain insight into oxazolyl's hybridization and aromaticity.

2. Experimental and theoretical methods

2.1. Synthesis of 2-D-oxazole

To demonstrate the exclusive formation of the C2-isomer of oxazolide under our experimental conditions, we synthesized 2-D-oxazole, *i.e.* oxazole deuterated at the C2 position. The following reaction scheme was used (Scheme 1).

The starting compound, 1,3-oxazole (1), was deuterated at the C2 position in the following manner. A solution of 1,3-oxazole (0.5 mL, 525 mg, 7.60 mmol) in ethyl ether (20 mL) was chilled in a dry ice and acetonitrile bath at -40 °C. After 10 min, the reaction mixture was treated with *t*-butyllithium (8 mL), yielding a yellow solution. The reaction mixture was stirred for 40 min, yielding a rust-color solution, which indicated a higher concentration of anion (2). The reaction mixture was then treated drop-wise with DCl in ether (5 mL). After stirring for 30 min, the reaction mixture was a salmon color. The mixture was partitioned with brine and ether, and then filtered through magnesium sulfate, yielding a faint yellow solution. Distillation in an oil bath at 55 °C recovered 8 mL, the first drop appearing at 30 °C. Upon NMR analysis, oxazole (1) underwent a 100% deuteration at the C2 position (3).

2.2. Anion photoelectron imaging spectroscopy

The mass-spectrometry and photoelectron imaging experiments were carried out using the negative-ion time-of-flight photoelectron imaging spectrometer described in detail previously.^{9,10} The anions were generated by introducing a neutral precursor gas mixture into



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Fig. 1 Possible isomers of the oxazolide anion and the corresponding oxazolyl radical formed upon the removal of H⁺ or H, respectively, from oxazole. All relative energy values are calculated at the B3LYP/aug-cc-pVQZ level of theory.



the high-vacuum ion source chamber through a pulsed supersonic nozzle (General Valve, Series 9) operated at a repetition rate of 50 Hz and a 30 psi backing pressure. The precursor gas mixture consisted of room-temperature oxazole vapor seeded in argon carrier gas, with minor O_2 and water contaminants from ambient air in the gas delivery lines. Negative ions were formed *via* slow secondary electron attachment following bombardment of the neutral precursors with high-energy (1 keV) electrons. Atomic oxygen anions generated from O_2 impurities assisted with the deprotonation/de-deuteration of oxazole. The anions were separated and characterized in the time-of-flight mass-spectrometer.

All oxazolide anions generated using the 2-D-oxazole precursor corresponded to 68 a.m.u. $(C_3H_2NO^-$, signifying the loss of D⁺ from 2-D-oxazole). No ions were observed at 69 a.m.u. (C_3HDNO^-) , which would correspond to the loss of H⁺ from either the C4 or C5 position in 2-D-oxazole. Supported by the knowledge that the deprotonation or de-deuteration of oxazole under our experimental conditions occurs selectively at the C2 position, the following photoelectron imaging studies of C2-oxazolide were carried out using the conventional (non-deuterated) oxazole precursor (Aldrich, Inc.).

The photodetachment of C2-oxazolide anions was performed at 355, 392, and 532 nm. The 392 nm light was obtained by frequency doubling the fundamental output of an amplified Ti:Sapphire laser (Spectra Physics; <1 mJ, 100 fs pulse width). The 532 and 355 nm laser beams were the second and third harmonics, respectively, of a Nd:YAG laser (Spectra Physics; 25 and 5 mJ, respectively, ~ 6 ns pulse duration). The laser beams were mildly focused using a 2 m focal-length lens positioned approximately 1.2 m before the laser–ion interaction region.

Details of the photoelectron¹¹ imaging^{12,13} assembly are described elsewhere.^{9,10} All photoelectron images in this work were recorded with the repeller, middle, and acceleration electrodes of the velocity-map¹⁴ imaging lens at -330, 0, and 900 V, respectively. The presented images correspond to multiple experimental runs, combined to span $\sim 10^6$ experimental cycles at each wavelength. The results were analyzed by means of the inverse Abel transformation¹³ using the BASEX software package.¹⁵

2.3. Theoretical methods

Electronic-structure calculations involving geometry optimizations were carried out at the density-functional (B3LYP) and coupledcluster (CCSD) levels of theory using the Gaussian 09 suite of programs.¹⁶ Calculations of the vertical detachment energy were also carried out using the equation-of-motion formalism combined with the coupled-cluster theory (EOM-IP-CCSD),¹⁷ as implemented in Q-Chem.¹⁸ A Franck–Condon simulation of the photoelectron spectrum was performed using the PESCAL program,^{19,20} with the anion and neutral geometries and frequencies calculated¹⁶ at the B3LYP/6-31+G* level of theory. Details of the mixed s–p model used in the analysis of the photoelectron angular distributions were reported previously.^{21–23} The canonical Hartree–Fock orbitals used in the modeling were computed with Gaussian.¹⁶

3. Results

The 355, 392, and 532 nm photoelectron imaging results for the C2-oxazolide anion, $C_3H_2NO^-$, are shown in Fig. 2. Each of the photoelectron images exhibits a series of rings, corresponding



Fig. 2 Raw and Abel-inverted photoelectron images (left and right halves, respectively) and the corresponding photoelectron spectra of $C_3H_2NO^-$ obtained at (a) 355 nm, (b) 392 nm, and (c) 532 nm. The laser polarization vector is vertical in the plane of the images, as indicated by the double arrow on the bottom right corner of (c).

to a partially resolved vibrational progression. The corresponding photoelectron spectra are plotted *versus* electron binding energy (eBE) alongside the images. The electron affinity is defined as the band origin, or lowest binding energy peak for the progression. The onset of this progression is best resolved in the 532 nm data, but some ambiguity exist concerning which of the peaks corresponds to the adiabatic EA of the oxazolyl radical, as some of the lower-eBE peaks may possibly be hot bands.

To resolve this uncertainty, we carried out a Franck-Condon simulation^{19,20} of the 355 nm spectrum. The anion and neutral geometries and frequencies calculated¹⁶ at the B3LYP/6-31+G* level were used in the analysis. The band origin and relative vibrational mode intensities were treated as adjustable parameters. Higher-level calculations do not necessarily yield better fits due to the approximations used in the modeling procedure. The simulated spectrum is shown in Fig. 2a in black, superimposed with the experimental spectrum (green). The Franck-Condon simulation allows for an unambiguous determination of the position of the band origin in all the experimental spectra. The simulated spectrum shown in Fig. 2a corresponds to $eBE_0 = 2.20 \text{ eV}$, in excellent agreement with the maximum position of the 532 nm origin peak in Fig. 2c at eBE $_0$ = 2.21 \pm 0.02 eV. The latter value, corresponding to the experimental determination rather than the simulation result, is assigned as the adiabatic electron affinity of oxazolyl, $EA(^{\bullet}C_{3}H_{2}NO) = 2.21 \pm 0.02 \text{ eV}.$

Two measurements of the band maximum (in the 355 and 392 nm data) yield the vertical detachment energy of C2-oxazolide, $VDE(C_3H_2NO^-) = 2.66 \pm 0.02$ eV. The average spacing between the vibrational peaks corresponds to 0.11 ± 0.01 eV



Fig. 3 Photoelectron anisotropy parameter values as a function of electron kinetic energy for the detachment from the oxazolide anion, C₃H₂NO⁻. Values are determined at 532 nm (green), 392 nm (blue), and 355 nm (red). Solid black curve: mixed s-p model prediction with $A = 0.75 \text{ eV}^{-1}$, B/A = 8/3, f = 0.64, and $\cos(\delta_2 - \delta_0) = 1$. Dashed red curve: Cooper–Zare central potential model prediction (Hanstorp's formulation)²⁸ with $\ell = 1$, $A = 0.75 \text{ eV}^{-1}$, and $\cos(\delta_2 - \delta_0) = 1$.

or 890 \pm 80 $\text{cm}^{-1},$ assigned to the in-plane C=N-C bending mode of the neutral radical.

Photoelectron angular distributions were determined over a spectral range of 0.10 eV for each partially resolved vibrational peak. The resulting anisotropy parameters vary from slightly negative ($\beta < 0$) at small electron kinetic energies (eKE), to slightly positive ($\beta > 0$) at larger eKEs, with a total range from $\beta = -0.15$ to $\beta = 0.27$. A plot of β as a function of eKE is shown in Fig. 3.

4. Discussion

4.1. Spectroscopic assignments and the electronic structure

The oxazolide anion studied is a closed-shell species resulting from deprotonation of the parent oxazole molecule at the C2 carbon site (Fig. 1). The ground-state nominal electron configuration of the anion is ${}^{1}A': \ldots (3a'')^{2}(15a')^{2}$, while that of the neutral radical is $X^{2}A': \ldots (3a'')^{2}(15a')^{1}$. As expected, oxazolyl is a σ radical, formed *via* the C–H bond fission in oxazole.

The band observed in the photoelectron spectra of $C_3H_2NO^$ is assigned to the above X^2A' state of C_3H_2NO . The experimentally determined electron affinity of oxazolyl is EA = 2.21 ± 0.02 eV (Fig. 2). This is the first determination of this important property. For comparison, the EA of C2-oxazolyl predicted by B3LYP/ aug-cc-pVQZ calculations (based on fully optimized anion and neutral structures, but without accounting for the zero-point vibrational energy corrections) is 2.22 eV (Fig. 1).

The most intense peaks in the 392 and 355 nm photoelectron spectra have maxima at 2.66 eV (Fig. 2). This result can be directly compared to theoretical predictions of the vertical detachment energy of the anion. B3LYP/aug-cc-pVQZ calculations yield a VDE of 2.83 eV. The EOM-IP-CCSD calculations with the 6-31++G** and 6-311++G** basis sets, using the respective B3LYP-optimized anion geometries, predict VDE = 2.68 and 2.73 eV, respectively.



Fig. 4 The predicted equilibrium geometries of the C2-oxazolide anion and the C2-oxazolyl neutral radical, based on B3LYP/aug-cc-pVQZ calculations. Bond lengths are in Angstroms.

The predicted equilibrium geometries of the anion and the neutral, based on B3LYP/aug-cc-pVQZ calculations, are shown in Fig. 4. The most significant geometry change upon photodetachment corresponds to the internal ring angles at the O, C2, and N atoms. The partially resolved vibrational structure in the photoelectron spectra in Fig. 2 has an average spacing of $890 \pm 80 \text{ cm}^{-1}$. This progression corresponds to one of the in-plane (*a'*) ring distortion modes. B3LYP/aug-cc-pVDZ calculations predict an 860 cm⁻¹ frequency mode corresponding predominantly to the opening of the C=N-C bending angle.

4.2. Photoelectron angular distributions

The observed PADs reflect the properties of the corresponding wavefunctions. Neglecting the electron correlation and relaxation effects, the PADs reflect the properties of the anion orbitals from which the electrons originate. In a more rigorous approach, the corresponding Dyson orbitals, representing the overlap between the anion and neutral wavefunctions, may be used to interpret the PADs.^{24,25} In detachment from groundstate anions, the character of the Dyson orbital is usually similar to that of the parent orbital. Our previous work²³ on pyridinide anion photodetachment indicated that the use of Dyson orbitals instead of canonical Hartree-Fock (HF) orbitals did not lead to significant changes in the analysis of the PADs. In the following we use the HF orbitals of oxazolide, but note that the Dyson orbitals can be adopted in this analysis at a minimal cost and without any substantive changes in the model formalism.



Fig. 5 (a) HOMO of C₃H₂NO⁻ (viewed from two different angles), as calculated at the B3LYP/aug-cc-pVDZ level of theory. (b) The mixed-character model function ψ_{sp} , composed of one s and one p-type function, with a fractional p character *f* = 0.64 and effective nuclear charge ζ = 3.18. Both (a) and (b) are plotted with an isosurface value of 0.08.

The 15*a*['] orbital of C2-oxozalide, from which the photodetached electrons originate, is plotted in Fig. 5a (the viewing frame has been rotated with respect to other figures for clarity). It is localized predominantly on the deprotonated carbon center. Because of the non-negligible contributions of both s and p type functions to this MO, the photodetachment process cannot be modeled using the Cooper–Zare central potential model.^{26–28} (The dashed red curve in Fig. 3 shows the centralpotential model prediction and the comparison with the experimental data is clearly unsatisfactory.) Instead, we apply the mixed s–p model,^{21,22} which was recently applied with success to photodetachment from the similar hybrid HOMO of pyridinide.²³

Describing the bound orbital as a superposition of one s and one p-type functions, the mixed s–p model predicts the following dependence of the anisotropy parameter β on eKE $\equiv \epsilon$:^{21,22}

$$\beta(\varepsilon) = \frac{2ZA\varepsilon + 2(A\varepsilon)^2 - 4A\varepsilon\cos(\delta_2 - \delta_0)}{ZA\varepsilon + 2(A\varepsilon)^2 + 1}.$$
 (1)

A is the coefficient describing the relative scaling of the p \rightarrow d and p \rightarrow s photodetachment channels, appearing in Hanstorp's formulation²⁸ of the Cooper–Zare equation^{26,27} for $\ell = 1$; $(\delta_2 - \delta_0)$ is the phase shift resulting from the outgoing d and s waves interacting with the neutral core, while *Z* is the s–p mixing parameter defined as:²²

$$Z = \frac{1-f}{f} \frac{B}{A}.$$
 (2)

In this definition, *f* is the fractional p character of the parent MO, while *B* is a coefficient describing the relative scaling of the s \rightarrow p and p \rightarrow s photodetachment channels,²¹ in a manner similar to *A* for p \rightarrow d and p \rightarrow s. Hence, *Z* describes the relative intensities of the s \rightarrow p and p \rightarrow s, d channels (*via B/A*), weighted by the contributions of the s and p components to the initial state, (1 - f)/f. Under certain assumptions, the *B/A* ratio for a 2s–2p mixed-character orbital (such as the 15*a*' HOMO of oxazolide in Fig. 5a), simplifies to *B/A* = 8/3.²²

To determine the fractional p character of the parent orbital, a model orbital ψ_{sp} is defined as a superposition of hydrogenic 2s and 2p functions (one of each) located on the deprotonated carbon center in oxazolide. The corresponding amplitudes are $\sqrt{1-f}$ and \sqrt{f} , respectively.^{21,22} The spatial extent of the hydrogenic functions is defined by an effective nuclear charge parameter ζ , assumed to be the same for the 2s and 2p contributions.²²

The least-squares fit of ψ_{sp} to the parent MO shown in Fig. 5a yields the optimal values of $\zeta = 3.18$ and f = 0.64. The effective charge of 3.18 compares favorably to the predictions of Slater's rules²⁹ of 3.25 and 2.9 for the n = 2 electrons in C and C⁻, respectively. As the excess charge in the oxazolide anion is partially delocalized, the ζ value is indeed expected to be an intermediate between those for the atomic neutral and the anion. An isosurface plot of the model orbital ψ_{sp} ($\zeta = 3.18$, f = 0.64) is shown in Fig. 5b. As expected, the dominant part of

the MO centered on C2, while missing the delocalized parts of the orbital.

Assuming that the *A* coefficient is the property of the atom on which the hybrid orbital is predominantly localized, the C⁻ value²² of $A = 0.75 \text{ eV}^{-1}$ is used to model the oxazolide PADs. A similar approach has been shown to work in the pyridinide case.²³ We caution, however, that oxazolyl has a higher electron affinity (EA = 2.21 ± 0.02 eV, per Fig. 2) than either pyridinyl (1.480 ± 0.006 eV)³⁰ or atomic carbon (1.262 eV).³¹ As *A* is related to the "size" of the detachment orbital,²⁸ its value could be smaller in the oxazolide case, corresponding to a more tightly bound (less diffuse) anion. On the other hand, the optimal model orbitals ψ_{sp} for pyridinide and oxazolide have similar effective nuclear charge values, $\zeta = 3.13$ and 3.18, respectively (fit to B3LYP/aug-cc-pVDZ MOs in both cases). Thus, the use of similar *A* values is justified.

The mixed s-p model prediction for oxazolide, calculated using eqn (1) with the above parameters, is superimposed with the experimental data in Fig. 3 (solid black curve). Neglecting the interactions between the outgoing partial waves and the remaining neutral core, we set $\cos(\delta_2 - \delta_0) = 1.^{23}$ It is stressed that this is a purely *ab initio* model prediction, not a fit to the experimental data. The model describes the experimental PADs for this system quite well, including the shallow dip in the $\beta(\varepsilon)$ dependence. From the trend in the angular distributions, we confidently assign the oxazolide anion HOMO of a 0.64 p character.

These results for oxazolide fit well within our broader investigation of organic heterocyclic anions. In particular, the discussion of the systematic trends observed for oxazolide, pyridinide,²³ thiophenide,³² furanide,³² and thiazolide is found elsewhere.³³

5. Conclusions

We have demonstrated selective deprotonation of oxazole at the C2 position. The photoelectron images and spectra of the resulting C2-oxazolide anion reflect the ground-state properties of the corresponding neutral oxazolyl σ radical. The adiabatic electron affinity of the radical is determined to be 2.21 \pm 0.02 eV. The spectra reveal a vibrational progression (890 \pm 80 cm $^{-1}$) corresponding to an inplane ring distortion mode. The analysis of the photoelectron angular distributions using the mixed s–p model indicates a 64% p character of the anion HOMO, consistent with the approximate sp² hybrid character nominally expected for this orbital.

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