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Photodetachment of Electrons from Large Molecular Systems. Pyrrolate Ion. Electron Affinity of C_4H_4N

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Abstract: The relative cross section for the gas-phase photodetachment of electrons has been determined for pyrrolate ions in the wavelength region 300-510 nm (4.13-2.43 eV). An ion cyclotron resonance spectrometer was used to generate, trap, and detect the negative ions, and a 1000-W xenon arc lamp with a grating monochromator was employed as the light source. The following quantities were determined: EA($C_4H_4N\cdot$) $\simeq$ 2.39 ± 0.13 eV; D(C_4H_4N-H) = 99 ± 6 kcal/mol. The electronic structure of pyrrolyl radical is discussed.

Photodetachment experiments, $A^- + h\nu \rightarrow A\cdot + e^-$, can provide information regarding electron affinities[3a] and electronic structures.[3b] Our recent examination of some rather complex anions suggests that much remains to be learned in this area.[3a] In order to explore further the cross-section behavior for detachment from delocalized systems and to study the influence of heteroatoms, we undertook a study of the pyrrolate anion $C_4H_4N^-$. This ion is an obvious analog to the previously examined $C_5H_5^-$; both are cyclic molecular ions with highly delocalized, aromatic π systems. The electronic structure of pyrrolate is additionally complicated by the presence of a localized, "nonbonding," σ pair of electrons.

In favorable cases, the onset of photodetachment (the vertical detachment energy) can be related to the adiabatic electron affinity. An estimate of the electron affinity can be made independently from bracketing reactions involving proton transfer in the gas phase:

$$AH + B^- \rightleftharpoons BH + A^- \qquad (1)$$

Neglecting the change in $\Delta S°$, the determination of the preferred direction of reaction 1 identifies the sign of $\Delta H°$. Given D for A-H and B-H, and EA for B·, we can then define limits for the electron affinity of A.

Experimental Section

Pyrrole (98%, Aldrich Chemical Co.) was distilled and stored at 4°. Nitrogen trifluoride, phosphine (Matheson), and hydrogen sulfide (Matheson) were used without further purification.

All experiments were performed on a Varian V-5900 icr spectrometer[4] with a modified square cell design.[3] Typical cell conditions employed high trapping voltages (2.5-1.6 V), moderate source drift voltages (0.7-0.2 V), and low analyzer drift voltages (less than 0.05 V). A 1000-W xenon arc lamp in conjection with a grating monochromator was employed as the light source. Gratings blazed at 300 nm (24.6-nm fwhm) and 1500 nm (23.8-nm fwhm) were used to investigate the short- and long-wavelength photodetachment behavior, respectively. Both gratings were used in the first order with long-wavelength pass filters to block light of higher orders. A conservative estimate of the total uncertainty in the wavelength calibration and zero grating position is 3 nm. An Eppley thermopile was used to measure the relative photon flux immediately after each run. Detailed explanations of the data collection and analyses have been previously reported.[3]

No additional ions were detected when irradiating with the xenon lamp and a 400-nm longpass filter. Conventional double resonance and pressure variation experiments were used to determine the preferred direction of various proton-transfer reactions.[4]

Pyrrolate ions were formed *via* two pathways. The first involved proton transfer to F^-, generated from NF_3 at 0.6-1.3 eV (electron energy minus trapping voltage). The total pressure[5] was 5-10 × 10^{-8} Torr during the experiments with the monochromator, although qualitatively the same results were obtained with long-wavelength pass filters at pressures up to 6 × 10^{-7} Torr. At total pressures exceeding 9 × 10^{-7} Torr, the photodetachment signal even with filters had significantly deteriorated.[6]

Results and Discussion

Figure 1 presents the results for photodetachment of $C_4H_4N^-$ (generated from F^- with pyrrole) in the range 300-510 nm. Four runs were averaged together, with an average maximum fractional signal decrease of 0.038. Standard deviations are approximately ±10% throughout the wavelength region studied. A linear least-squares fit to all the data yields an intercept of 519 ± 3 nm [2.389 ± 0.014 eV (55.1 ± 0.3 kcal/mol)].

Several reactions were studied with the purpose of estimating the electron affinity of the pyrrolyl radical indepen-

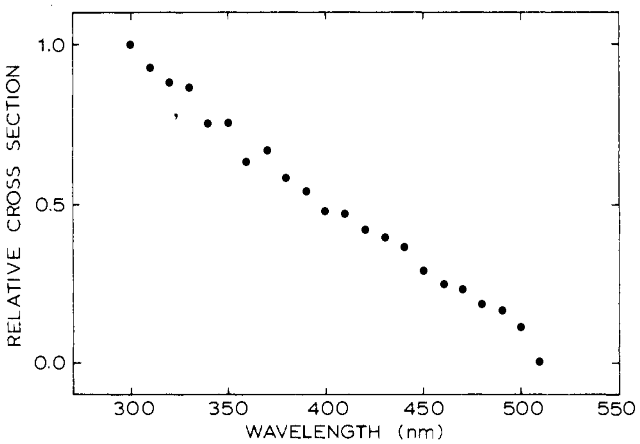

Figure 1. Relative cross section for the photodetachment of $C_4H_4N^-$ generated from proton abstraction by F^-. Average of four runs; bandwidth is 24.5-nm fwhh. Typical standard deviations are ±10%. The energy range is 4.13–2.43 eV.

dently of the photodetachment experiments. Total pressures

$$\mathrm{SH^- + C_4H_5N \longrightarrow C_4H_4N^- + H_2S} \tag{2}$$

$$n\text{-}\mathrm{C_4H_9S^- + C_4H_5N \longrightarrow C_4H_4N^-} + n\text{-}\mathrm{C_4H_9SH} \tag{3}$$

$$\mathrm{CH_3S^- + C_4H_5N \longrightarrow C_4H_4N^- + CH_3SH} \tag{4}$$

$$\mathrm{PH_2^- + C_4H_5N \longrightarrow C_4H_4N^- + PH_3} \tag{5}$$

$$\mathrm{F^- + C_4H_5N \longrightarrow C_4H_4N^- + HF} \tag{6}$$

were varied from 5×10^{-8} to 2×10^{-6} Torr. Reactions 2 and 3 did not proceed toward the right to any detectable extent, whereas reactions 4–6 were facile. The failure to observe reaction 3 permits a lower limit to be placed on the difference between the nitrogen-hydrogen bond strength (D) and the electron affinity (EA) of the pyrrolyl radical, while the occurrence of reaction 4 permits an upper limit to be placed on this difference:

$$D(\mathrm{C_4H_4N{-}H}) - \mathrm{EA}(\mathrm{C_4H_4N\cdot}) \geq 1.82 \pm 0.09\ \mathrm{eV}\ (42 \pm 2\ \mathrm{kcal/mol})$$

$$D(\mathrm{C_4H_4N{-}H}) - \mathrm{EA}(\mathrm{C_4H_4N\cdot}) \leq 1.99 \pm 0.09\ \mathrm{eV}\ (46 \pm 2\ \mathrm{kcal/mol})$$

The following thermochemical data were used: $D(n\text{-}\mathrm{C_4H_9S{-}H}) \approx D(\mathrm{CH_3S{-}H}) \approx 88$ kcal/mol;[7] EA(N-C_4H_9S) = 45.8 ± 1.5 kcal/mol;[8] EA($CH_3S\cdot$) = 42.1 ± 1.5 kcal/mol.[8]

Using the photodetachment intercept as an estimate of EA($C_4H_4N\cdot$) yields an N-H bond dissociation energy in pyrrole between 97 ± 4 and 101 ± 4 kcal/mol. This is slightly higher than that known for dimethylamine[9] (95 ± 2 kcal/mol), a difference which might be expected in going from systems approximately tetrahedral to those approximately trigonal.

It is necessary to know both the initial state of the ion and final state of the neutral before a photodetachment threshold can be definitely associated with the adiabatic electron affinity. One might assume that there would be good Franck-Condon factors between the pyrrolate ion and the pyrrolyl radical, especially if both structures resemble that of pyrrole itself. For comparison, there are no significant vibrational progressions in the electronic spectrum of pyrrole.[10] The vibrational frequencies[11] of the pyrrolate ion, measured as its potassium salt, differ only slightly from those of pyrrole.[11,12] Consequently, we would expect that removal of either a proton or a hydrogen atom would have little effect on the overall ring geometry. The lowest fundamental of the pyrrolate ion, 558 cm^{-1}, corresponds to 13 nm at 519 nm; hence the resolution is insufficient to distinguish vibrational fine structure, corresponding to $\Delta v_i \neq 0$.

In summary, the results of the proton-transfer reactions, the limited resolution, and the expected similarity between the ion and neutral geometry suggest that the photodetachment threshold is a good estimate of the electron affinity of the pyrrolyl radical:

$$\mathrm{EA}(\mathrm{C_4H_4N\cdot}) \approx 2.39 \pm 0.12\ \mathrm{eV}\ (55 \pm 3\ \mathrm{kcal/mol})$$

where the error is a reflection of the instrumental bandwidth.

In considering photodetachment of an electron from an anion such as pyrrolate, we can imagine loss of either a π or a "non-bonding" σ electron. Normally, it is assumed that the electron affinity will correspond to loss of an electron from the highest occupied MO in the anion. Analysis of this sort often serves as the basis for assignment of energies from photoelectron spectra, although the approach has been criticized.[13] That the usual assumption can break down is shown clearly by the classic examples of transition metal atoms and ions, in which orbital orderings are sensitive to nuclear charge. For example, the 4s orbitals lie below the 3d in some of the neutrals, but the s electrons are lost in the lowest ionizations.

The same phenomenon may well be occurring in pyrrolate. A semiempirical (CNDO/2) calculation[14] suggests that the π electrons in pyrrolate ion are the most weakly bound, the highest occupied orbitals being $6B_2^2\ 9A_1^2\ 2B_1^2\ 1A_2^2$. (The $9A_1$, is the "non-bonding" orbital, the B_1 and A_2 are π.) This ordering is in accord with arguments that the s character in the A_1 orbital should stabilize it. Although we should, therefore, expect that the radical will have lost a π electron, an INDO open-shell calculation[14] shows $6B_2^2\ 9A_1^1\ 2B_1^2\ 1A_2^2$. If restricted in a closed-shell calculation, the ordering is $6B_2^2\ 2B_1^2\ 1A_2^2\ 9A_1^1$, again suggesting that the odd electron is σ rather than π. Thus, the calculations suggest that reordering occurs when the electron is lost, producing a σ radical. The calculation presumably reflects a substantially greater intraorbital electron repulsion in the σ orbital compared with the more diffuse π orbitals. This effect is enhanced by the added stability of the closed π shell. While calculations of this type may not be completely reliable, they do suggest the likelihood of orbital reordering in systems with nonbonded and π electrons, and such reordering may be responsible for some of the difficulties encountered in analyzing photoelectron spectra in systems with both types of electrons.

The thermochemistry derived from our experiments also suggests a σ radical. If the pyrrolyl radical is σ, it should have about the same empirical resonance energy as pyrrole, and thus pyrrole would have a normal N-H bond strength. If, however, the pyrrolyl radical is π, the N-H bond in pyrrole would be lower by the additional stabilization in the radical. Thus, the agreement between the N-H bond strength derived from our experiments and that expected for a normal system[9] is consistent with a σ radical.

The threshold behavior of photodetachment cross sections can provide information about electronic structure.[3,15] As in the case of cyclopentadienide,[3a] the cross section for pyrrolate rises in a nearly linear fashion over a large energy interval. Table I compares the relative photodetachment cross section, σ, of $C_4H_4N^-$, $C_5H_5^-$, $CH_3C_5H_4^-$ fitted to the following expansion in the energy of the detached electron:

$$\sigma = (E)(E_k)^b(a_0 + a_1E_k + a_2E_k^2 + a_3E_k^3 + a_4E_k^4)$$

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Table I. Least-Squares Fit of Data[a]

Parameter	$C_4H_4N^-$	$C_5H_5^-$	$CH_3C_5H_4^-$
E_0	2.317 eV	1.825 eV	1.625 eV
b	1.125	1.344	1.727
a_0	0.407	0.547	0.426
a_1	−0.346	−0.502	−0.408
a_2	0.147	0.175	0.157
a_3	−0.0191	−0.0178	−0.0249
a_4	−0.00230	−0.00110	−0.00112
Rms error	0.029	0.0077	0.0018
Maximum error	0.055	0.013	0.0031

[a] Data fitted to the equation, $\sigma = (E)(E_k)^b(a_0 + a_1E_k + a_2E_k^2 + a_3E_k^3 + a_4E_k^4)$.

where E is the photon energy, E_k is the energy of the detached electron ($E - E_0$), E_0 is the threshold energy, and b and the *a's* are empirical constants.[16]

In contrast to our earlier argument, the similarity in cross sections might be taken to suggest loss of π electron from pyrrolate ion, with the larger value of E_0 resulting from the greater electronegativity of nitrogen.[17,18] However, because the threshold theory has not been worked out in detail for polyatomics, and in particular because loss of an electron may not be occurring from the HOMO, we cannot fully interpret the threshold behavior.

No photodetachment to longer wavelengths was detected when $C_4H_4N^-$ was generated from F^- by proton abstraction. However, when generated from CH_3O^--CH_3ONO, weak photodetachment of $C_4H_4N^-$ occurred at wavelengths beyond the photodetachment threshold of CH_3O^-.[8] This photodetachment loss was too small to investigate in detail. To explore this observation more thoroughly, a careful examination for a possible long-wavelength photodetachment cross section for $C_4H_4N^-$ was initiated. To maximize what was obviously a small cross section, $C_4H_4N^-$ was generated directly from pyrrole by dissociative electron capture at very low pressure. Attempts to improve the leaving group[19] and thus enhance the signal by synthesizing *N*-nitrosopyrrole were unsuccessful. The consistently weak negative ion signal obtained permitted adequate data at long wavelength to be taken with the monochromator only once. A linear least-squares fit of these data near threshold yields an intercept of 1592 ± 14 nm; 0.778 ± 0.008 eV (17.9 ± 0.2 kcal/mole). There was no change in the $C_4H_4N^-$ signal when either the source or analyzer region was irradiated with the appropriate frequency of sufficient amplitude to eject H^-. Furthermore, the cross section did not resemble the photodetachment cross section for H^-.[15] Hence, this long-wavelength photodetachment signal was attributed to an ion with the same *m/e* ratio as pyrrolate.

This long-wavelength photodetachment threshold requires explanation. If this threshold (18 kcal/mol) corresponds to the electron affinity of pyrrolyl radical, then the N-H bond strength in pyrrole must be 60-64 kcal/mol using the thermochemical cycle described above. Such an anomalously low N-H bond energy implies an additional 30-kcal/mol stabilization in pyrrolyl radical relative to pyrrolate, which seems inordinately large. Thus, it is doubtful that the long-wavelength threshold is associated with the loss of an electron from the ground state of pyrrolate.

Vibronic excitation of the ion is also unlikely to account for this threshold. The relatively long trapping times (*ca.* 1 sec) generally assure complete relaxation.

A third possibility is that the long-wavelength threshold corresponds to photodetachment of an isomeric species of *m/e* 66. It is expected that such a species would have a photodetachment spectrum considerably different than that of the pyrrolate ion.[20] The data for the long-wavelength threshold do not warrant detailed analysis, but it is noteworthy that the cross section does turn over and flatten out *ca.* 300 nm from threshold. This behavior resembles that of small binary hydrides and implies similar geometries for both the neutral and negative ion. The long-wavelength photodetachment cross section rises over approximately twice the energy range observed[21] for NH_2^- and has a threshold only 0.038 eV higher. This similarity suggests that the long-wavelength threshold may be due to an acyclic isomer of *m/e* 66. For comparison, flash-photolyzed pyrrole, allyl cyanide, and crotyl nitrite yield identical spectra, corresponding to a $C_4H_4N\cdot$ radical.[22]

Thus, we assume that short-wavelength threshold corresponds to the electron affinity of pyrrolate; the long-wavelength threshold must be due to some other source, probably an isomeric species.

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