solution for amino acid synthesis yet absent in the vapor phase because of its rapid photolysis. Ammonia would still have been subject to rapid photodestruction so that this model would only have been valid for a short time on the geological time scale.

Finally, it should be noted that some of the starting materials and photoproducts in our work have been detected in interstellar space.[37] For example, water, methanol, formaldehyde, and acetaldehyde have been identified. Although our laboratory synthesis of aldehydes, ketones, and alcohols was carried out under conditions which differ appreciably from those in the interstellar medium, our results provide some support for the hypothesis that the interstellar molecules were formed photochemically.[37]

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Photodetachment of Electrons from Phenoxides and Thiophenoxide

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Abstract: The relative cross section for the gas phase photodetachment of electrons has been determined for several substituted phenoxides and thiophenoxide in the wavelength region 300-530 nm (4.13-2.34 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: $EA(o\text{-}CH_3C_6H_4O\cdot) \approx EA(C_6H_5O\cdot) \leq 2.36 \pm 0.06$ eV, $EA(o\text{-}ClC_6H_4O\cdot) \leq 2.58 \pm 0.08$ eV, $EA(C_6H_5S\cdot) \leq 2.47 \pm 0.06$ eV. It is suggested that a short wavelength portion of the photodetachment spectrum is the result of electronic excitation of the negative ions, followed by autodetachment.

Recent photodetachment experiments have indicated that complex molecular ions can exhibit unusual behavior. This appears to be particularly true for delocalized systems, such as $C_5H_5^-$ and $C_4H_4N^-$.[3,4] The photodetachment cross section of an anion can provide information about a variety of molecular properties. The threshold yields a vertical electron detachment energy, which in favorable cases also represents the electron affinity of the corresponding radical. Abrupt changes in the photodetachment cross section can arise from transitions to excited states,[5] thus, transition energies may be determined. In the present paper, we present a study of thiophenoxide and a series of phenoxide anions. Photodetachment cross sections here display well defined thresholds and also show short wavelength structure, which is interpreted as excitation to an autodetaching excited state of the anion. This represents a photochemical process of a molecular anion which has not, to our knowledge, been reported previously.[6,7]

Phenoxides are an important series of compounds to study for several reasons. (1) The gas phase acidity of several monosubstituted phenols has been determined;[8] it is of interest to see whether the differences in relative acidity are due to differences in the hydroxyl bond dissociation energy, the electron affinity of the corresponding phenoxy radical, or a combination of the two. (2) Phenoxide possesses both extensive, π-delocalized molecular orbitals and more highly localized nonbonding orbitals; different photodetachment cross sections might be expected for electrons in the two different orbitals. (3) In solution phenoxide ions exhibit a near uv absorption spectrum; consequently it is of interest to determine the gas phase photodetachment in the same spectral region.

Experimental Section

All the phenols and thiophenol (Aldrich Chemical Co.) were used without further purification. All experiments were performed on a Varian V-5900 ICR spectrometer with a modified square cell design.[9] Typical cell conditions employed high trapping voltages (1.30-2.40 V), moderate source drift voltages (0.10-0.60 V), and low analyzer drift voltages (less than 0.05 V). Typical pressures were 9×10^{-8} to 1.5×10^{-6} Torr;[10] under these conditions, ions were trapped up to several seconds.[11]

All ions were formed by dissociative electron capture at the lowest energy resonance capture maximum. For $C_6H_5O^-$, o-$CH_3C_6H_4O^-$, and $C_6H_5S^-$ this maximum was nominally 0.7-2.0 eV (electron energy minus trapping voltage). For o-$ClC_6H_4O^-$ and m-$ClC_6H_4O^-$ higher energies were used, 6.0-6.7 eV, as only Cl^- was formed at the lowest resonance capture maximum. There was little or no Cl^- formed from o-ClC_6H_4OH at the higher electron energies; ion ejection experiments[12] demonstrated that Cl^- did not affect either chlorophenoxide photodetachment spectrum.

Experiments with long wavelength pass filters demonstrated a low intensity chlorophenoxide photodetachment signal at wavelengths longer than 1150 nm. Other ions studied in this laboratory have shown similar behavior when formed at higher electron energies. This observation is consistent with H^- being the precursor for at least some of the chlorophenoxide formed. Irradiation at longer wavelengths would lead to photodetachment of H^- with a subsequent decrease in $ClC_6H_4O^-$; this decrease would appear as an apparent photodetachment of $ClC_6H_4O^-$. However, this long wavelength tail could not be detected with the monochromator. Other ions exhibiting this behavior yield identical photodetachment cross sections at low and high electron energies;[3] for example, the OH^- photodetachment cross section[13] is obtained even though H^-/H_2O is the precursor.

Long wavelength photodetachment signals with the filters were also obtained for $C_6H_5O^-$, $C_6H_5S^-$, and o-$CH_3C_6H_4O^-$ formed at a higher dissociative electron capture maximum (9.0-9.5 eV). Ion ejection experiments did indicate a signal decrease corresponding to H^- ejection. However, the photodetachment cross sections obtained with the monochromator were identical to those obtained at lower electron energies (where there was no evidence for H^-). Consequently, we believe that these long wavelength detachment results for the chlorophenoxides are not due to photodetachment of chlorophenoxide itself. In no cases were additional ions observed when irradiating with the light.

A 1000 W xenon or xenon-mercury arc lamp in conjunction with a grating monochromator was employed as the light source. A grating blazed at 300 nm was used in the first order with various matched slits, resulting in bandwidths of 5.8, 9.6, 14.4, or 24.6 nm (full width at half maximum). Long wavelength pass filters were used to block light of higher orders. A conservative estimate of the total uncertainty in the wavelength calibration and zero position is 3.0 nm. An Eppley thermopile was used to measure the relative photon flux immediately after each run.

Detailed explanations of the data collection and analysis have been previously reported.[9,14] Conventional double resonance and pressure variation experiments were used to determine the preferred direction of various proton transfer reactions.[15]

Results and Discussion

Figures 1-5 present the results for the photodetachment of $C_6H_5O^-$, o-$CH_3C_6H_4O^-$, o-$ClC_6H_4O^-$, m-$ClC_6H_4O^-$, and $C_6H_5S^-$, respectively. The average maximum fractional signal decrease was 0.19, 0.25, 0.084, 0.060, and 0.13, respectively. Cross sections identical to those presented were obtained for $C_6H_5O^-$, o-$CH_3C_6H_4O^-$, and $C_6H_5S^-$ using the xenon or xenon-mercury lamp with a bandwidth of 5.8 nm; the cross section for phenoxide-*2,4,6-*d_3 was also identical to that obtained for phenoxide itself.

Linear least-squares fits near threshold yield the following intercepts for $C_6H_5O^-$, o-$CH_3C_6H_4O^-$, o-$ClC_6H_4O^-$, and $C_6H_5S^-$: 525.7 ± 2.0 nm (2.36 ± 0.01 eV), 540.0 ± 4.7 nm (2.30 ± 0.02 eV), 480.0 ± 4.0 nm (2.58 ± 0.02 eV), and 501.0 ± 1.8 nm (2.47 ± 0.01 eV), respectively. There was insufficient signal-to-noise to investigate the threshold region of m-$ClC_6H_4O^-$; the short wavelength cross section is shown.

To bracket independently the electron affinities of $C_6H_5O\cdot$ and $C_6H_5S\cdot$, the following proton transfer reactions were investigated:[16]

$$Br^- + C_6H_5SH \rightarrow HBr + C_6H_5S^- \tag{1}$$

$$Cl^- + C_6H_5SH \rightarrow HCl + C_6H_5S^- \tag{2}$$

$$HS^- + C_6H_5SH \rightarrow H_2S + C_6H_5S^- \tag{3}$$

$$Br^- + C_6H_5OH \rightarrow HBr + C_6H_5O^- \tag{4}$$

$$Cl^- + C_6H_5OH \rightarrow HCl + C_6H_5O^- \tag{5}$$

$$HS^- + C_6H_5OH \rightarrow H_2S + C_6H_5O^- \tag{6}$$

$$CN^- + C_6H_5OH \rightarrow HCN + C_6H_5O^- \tag{7}$$

Reactions 1, 4, and 5 did not occur to any appreciable extent. Reaction 2 could be driven to the right and hence was not greatly endothermic, while reactions 3, 6, and 7 were facile. Thus, the following limits can be placed:[17]

$$1.68 \text{ eV} < \mathrm{EA}(C_6H_5S\cdot) \lesssim 2.39 \text{ eV}$$

$$2.28 \text{ eV} < \mathrm{EA}(C_6H_5O\cdot) < 3.00 \text{ eV}$$

The following thermodynamic quantities were used: $DH°$(HS-H) = 3.90 eV,[18] EA(HS·) = 2.319 eV,[19] $DH°$(H-Cl) = 4.47 eV,[20] EA(Cl·) = 3.613 eV,[21] $DH°$(C_6H_5S-H) = 75 kcal/mol,[18] and $DH°$(C_6H_5O-H) = 89 kcal/mol.[22]

The agreement (within experimental error) between the limits obtained from the proton transfer reactions and the photodetachment thresholds suggests that the latter are likely to be good estimates of the electron affinities of the corresponding neutral radicals. Two assumptions are implicit in estimating electron affinities with photodetachment thresholds: (1) the ions are in the ground vibrational state; (2) the geometries of the ion and neutral are similar, hence implying good Franck-Condon factors between the two surfaces.[1,23]

Ions in the ICR are usually considered to be thermalized, even when formed under very exothermic conditions with appreciable amounts of internal energy. The long trapping conditions generally provide sufficient time for collisions and spontaneous emission to thermalize the ions. However, even at room temperature a large fraction of the phenoxide ions will not be in the ground vibrational state.[24] Such thermal excitation might be expected to give rise to hot bands, with corresponding shifts in the photodetachment threshold. The bandwidth employed in these experiments is too large to resolve such shifts or any other vibrational fine structure.

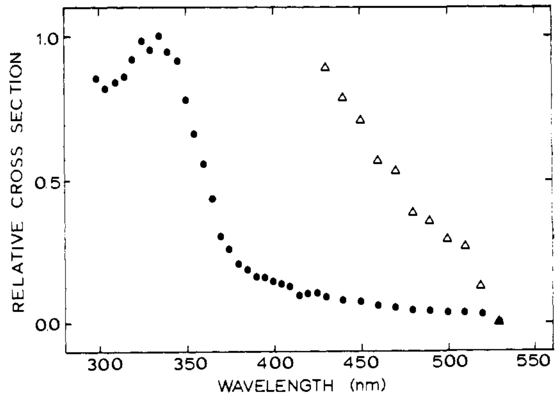

Figure 1. Relative cross section for the photodetachment of $C_6H_5O^-$ with the xenon lamp and a bandwidth of 14.4 nm (●), multiplied 10× (△). The results of eight runs are averaged; typical standard deviations are ±4% at the shorter wavelength, gradually increasing to ±20% near threshold.

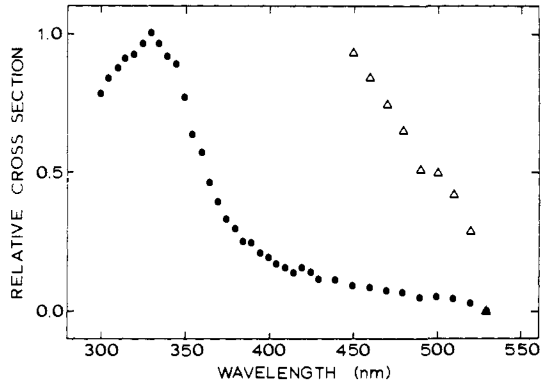

Figure 2. Relative cross section for the photodetachment of *o*-$CH_3C_6H_4O^-$ with the xenon lamp and a bandwidth of 9.6 nm (●), multiplied 10× (△). The results of three runs are averaged; typical standard deviations are ±3% at the shorter wavelengths, gradually increasing to ±12% near threshold.

Hence, experimentally, the vertical detachment energy is expected to be greater than or equal to the electron affinity. It is unlikely that the geometries are very dissimilar;[24b,25] thus, the photodetachment threshold may be taken as an upper limit to the electron affinity, with errors reflecting the bandwidth.

$$\mathrm{EA}(o\text{-}CH_3C_6H_4O\cdot) \approx$$
$$\mathrm{EA}(C_6H_5O\cdot) \leq 2.36 \pm 0.06\ \mathrm{eV}\ (54.4 \pm 1.4\ \mathrm{kcal/mol})$$
$$\mathrm{EA}(o\text{-}ClC_6H_4O\cdot) \leq 2.58 \pm 0.08\ \mathrm{eV}\ (59.5 \pm 1.8\ \mathrm{kcal/mol})$$
$$\mathrm{EA}(C_6H_5S\cdot) \leq 2.47 \pm 0.06\ \mathrm{eV}\ (57.0 \pm 1.4\ \mathrm{kcal/mol})$$

It is of interest to compare the electron affinities with the gas phase acidity of the corresponding phenol: *o*-ClC_6H_4OH > *o*-$CH_3C_6H_4OH$ > C_6H_5OH (chlorophenols are stronger acids in solution also).[26] The ΔG°_{298} (kcal/mol) for the gas phase reaction between phenol and the substituted phenoxide is 0.3, 4.6, and 6.1 kcal/mol for *o*-methyl, *o*-chloro, and *m*-chloro, respectively.[8] The electron affinity of the substituted phenoxy radical appears to be the dominant factor in determining the relative acidity of the substituted phenols. In contrast, similar electron affinities but a much weaker sulfur hydrogen bond imply that thiophenol is a stronger acid than phenol; this is also the order in solution.[26a]

The most noteworthy feature of the photodetachment cross sections in Figure 1-5 is the sharply rising portion in the near uv. Based on the proton-transfer reactions, it is apparent that the lower intensity, nearly linear cross section at longer wavelengths (>400 nm) corresponds to photodetachment of an electron from the highest occupied molecular orbital. Such linearly rising cross sections have been previously observed,[27] particularly for delocalized ions.[3,4]

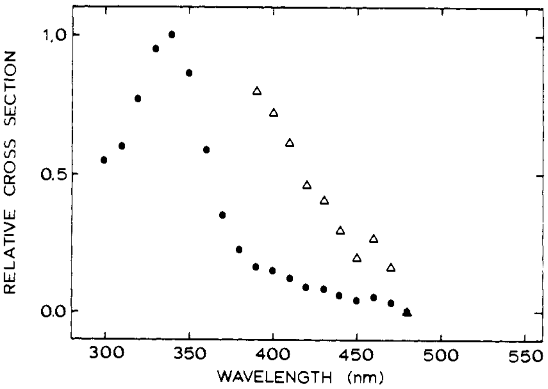

Figure 3. Relative cross section for the photodetachment of *o*-$ClC_6H_4O^-$ with the xenon lamp and a bandwidth of 14.1 nm (●), multiplied 15× (△). The results of six runs are averaged; typical standard deviations are ±5% at shorter wavelengths, gradually increasing to ±20% near threshold.

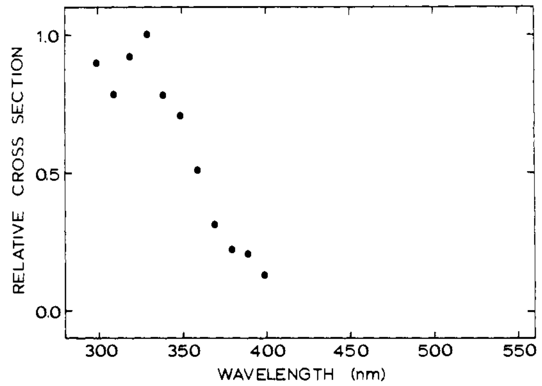

Figure 4. Relative cross section for the photodetachment of *m*-$ClC_6H_4O^-$ with the xenon lamp and a bandwidth of 24.1 nm. The results of three runs are averaged; typical standard deviations are ca. ±10% throughout.

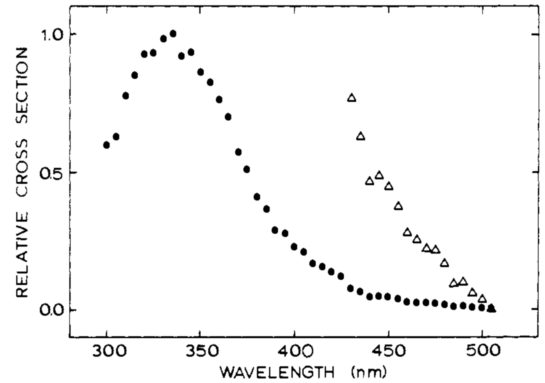

Figure 5. Relative cross section for the photodetachment of $C_6H_5S^-$ with the xenon lamp and a bandwidth of 9.6 nm (●), multiplied 10× (△). The results of seven runs are averaged; typical standard deviations are ±4% near the maximum, gradually increasing to ±15% near threshold and toward 300 nm.

Removal of an electron from a lower energy orbital, resulting in an excited electronic state of the neutral, could result in a sharp rise in the relative photodetachment cross section. However, there are few examples of photodetachment cross sections subsequently decreasing so dramatically with increasing photon energy.[5a,6,7] Furthermore, the energy separation between the photodetachment threshold and the onset of the sharp rise is less than 1 eV. The lowest reported transition in the phenoxy radical is ca. 2.0 eV.[28] Thus, the maximum in the photodetachment cross section cannot be attributed to production of electronically excited phenoxy radical, as it occurs about 1 eV too low in energy.

The shapes of the lowest energy uv absorption spectra of the neutral phenols used in this study are nearly identical,[29] with thiophenol being only slightly different.[30,31] The photodetachment cross sections of all five ions are also very similar. In addition, the photodetachment cross section maxima are shifted to slightly longer wavelength relative to the solution spectra[24b,30,32] as might be expected.[33,34] We believe that an attractive explanation of the short wavelength structure is electronic excitation of the ion, followed by autodetachment of an electron. This is consistent with the appearance of the photodetachment spectrum as a superposition of a broad, gradually rising cross section and an electronic absorption maximum. Electronic excitation has been invoked previously in photodissociation of positive ions.[35]

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