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Enolate Structure and Electron Affinity

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Photodetachment cross sections for a series of cyclic enolates were measured using a continuous wave (CW) ion cyclotron resonance instrument to generate and detect the ions. We report electron affinities for the radicals corresponding to the removal of the extra electron from the following anions: 2-methylcyclopent-1-enolate, 3-methylcyclopent-1-enolate, 4-methylcyclopent-1-enolate, 5-methylcyclopent-1-enolate, 2-methylcyclohex-1-enolate, 3-methylcyclohex-1-enolate, 4-methylcyclohex-1-enolate, 4-ethylcyclohex-1-enolate, 5-methylcyclohex-1-enolate, and 6-methylcyclohex-1-enolate. Some of these anions are mixed with their tautomers, derived from deprotonation of the parent ketone; the consequences of this are analyzed. The effect of alkylation on the electron affinities is discussed. The effect of vibrational modes on the lifetimes of the dipole-bound states of 4-methylcyclohex-1-enolate and 4-ethylcyclohex-1-enolate is discussed.

Introduction

Enolate anions play a major role in synthetic chemistry. A solid understanding of the intrinsic chemistry of these species can aid in the design and implementation of reaction schemes. Solution studies of enolate anions, however, can be difficult to interpret because of solution effects and counterion effects; it is not unusual for small differences in stability between species to be overwhelmed by solvent effects.[1] In this work, we explore the effect of structure on the solvent-free energetics of enolate ions.

The electron affinity (EA) is one aspect of the energetics in a series of related compounds that is greatly influenced by structure. The electron affinity of a radical is the energy difference between the radical and the anion formed by adding an electron to the radical. When the anion is more stable than the radical, the EA is positive. The electron affinity can be determined by photodetachment studies and, along with the proton affinity of the species, can be used in a thermochemical cycle to derive homolytic bond dissociation energies. Photodetachment studies can also give information about the autodetachment mechanisms and autodetachment rates of excited anions.[2,3]

Another interesting effect of subtle changes in structure is the presence or absence of sharp resonances, often only a few nanometers wide, near thresholds in photodetachment spectra. These are now known to be the result of a transition to a dipole-bound electronic state, which has a larger optical cross section than that of the direct transition to the continuum. A dipole-bound state is an anion where an electron is bound by the dipole to a neutral molecule's core. This excited state must have enough energy to autodetach to be observed, so it must be in a rotationally or vibrationally excited state (Figure 1). In the cases studied here, the dipole state is within a few wavenumbers of the photodetachment threshold and the autodetaching states at threshold are rotationally excited. Resonances above the threshold involve autodetachment from vibrationally excited states.[4] Curiously, under our experimental conditions, many species have observable dipole-bound states whereas other electronically similar species do not.

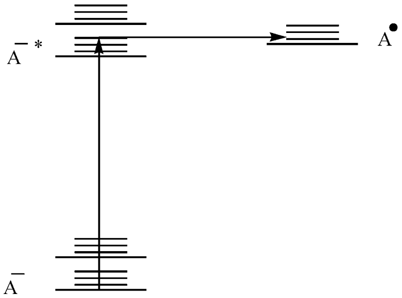

Figure 1. Photoexcitation to a rotationally excited dipole-bound state (A^{-}*) which undergoes autodetachment to the radical.

In 1947, Fermi and Teller first predicted the existence of dipole-bound states.[5] In dipole-bound states, it is believed that the electron occupies a very diffuse orbital; the electron typically resides 50−200 Å away, and as a result, the geometry is perturbed very little from the geometry of a completely separated neutron and electron.[6−10] In addition, the extra electron is bound very weakly; typically, the binding energy is between 5 and 300 cm^{-1}.[6−9,11]

In this work, we investigated the stabilities of cyclic enolate anions compared to those of their corresponding radicals in the gas phase. The effects of alkyl substitution on small cyclic enolates were studied, using both low- and high-resolution photodetachment spectroscopy. In addition, the effect of vibrational excitation of the dipole-bound state's lifetime was investigated for the 4-methylcyclohex-1-enolate and 4-ethylcyclohex-1-enolate anions.

Experimental Section

Chemicals. Nitrogen trifluoride was purchased from Ozark-Mahoning, and all other compounds were purchased from Aldrich, Inc. 4-Methylcyclohexanone (>97% purity) and 4-ethylcyclohexanone (97%) were purchased from Aldrich and were

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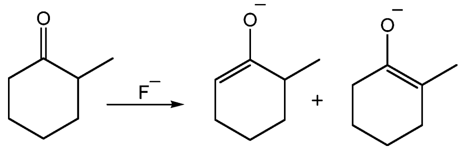
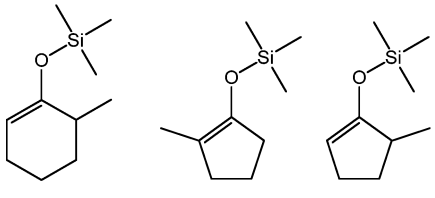
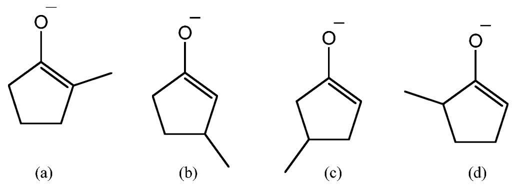


Figure 2. 2-Methylcyclohexanone and the two enolate ions formed by deprotonation.



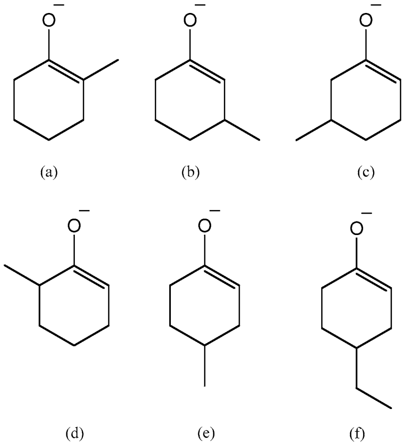
(**I**) (**II**) (**III**)

Figure 3. Silyl enol ethers 6-methylcyclohex-1-enol trimethylsilyl ether (**I**), 2-methylcyclopent-1-enol trimethylsilyl ether (**II**), and 5-methylcyclopent-1-enol trimethylsilyl ether (**III**).



(a) (b) (c) (d)

Figure 4. Cyclopent-1-enolate derivatives (a) 2-methylcyclopent-1-enolate, (b) 3-methylcyclopent-1-enolate, (c) 4-methylcyclopent-1-enolate, and (d) 5-methylcyclopent-1-enolate.



(a) (b) (c)

(d) (e) (f)

Figure 5. Cyclohex-1-enolate derivatives (a) 2-methylcyclohex-1-enolate, (b) 3-methylcyclohex-1-enolate, (c) 5-methylcyclohex-1-enolate, (d) 6-methylcyclohex-1-enolate, (e) 4-methylcyclohex-1-enolate, and (f) 4-ethylcyclohex-1-enolate.

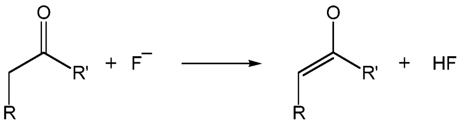
used as precursors to generate 4-methylcyclohex-1-enolate and 4-ethylcyclohex-1-enolate. 6-Methylcyclohex-1-enol trimethylsilyl ether (**I**), 5-methylcyclopent-1-enol trimethylsilyl ether (**III**), and 2-methylcyclopent-1-enol trimethylsilyl ether (**II**) were synthesized. They were used as precursors to generate 6-methylcyclohex-1-enolate, 2-methylcyclopent-1-enolate, and 5-methylcyclopent-1-enolate, respectively. The deprotonation products of 2-methylcyclohexanone, 3-methylcyclohexanone, 2-methylcyclopentanone, and 3-methylpentanone were a mixture of two enolate anions from each species. An example is shown in Figure 2. Before introduction into the reaction cell, all compounds were subjected to multiple freeze−pump−thaw cycles to degas them and to remove volatile impurities. In all cases, the only peaks seen in the mass spectrum were those of fluoride and the peak corresponding to deprotonation.

The 6-methylcyclohex-1-enol trimethylsilyl ether (**I**, Figure 3) was synthesized from 2-methylcyclohexanone (>97% purity) using a method similar to that reported by House et al.[12] The 6-methylcyclohex-1-enol trimethylsilyl ether was prepared by adding 5.5 mL (45 mmol) of 2-methylcyclohexanone to a lithium diisopropylamide solution over a 10 min period. The lithium diisopropylamide solution was prepared by adding 5.5 g (55 mmol) of diisopropylamine to about 50 mL of a 1.0 M solution of *n*-butyllithium in ether, cooled to 0 °C. A quenching solution, prepared from 25 mL of 1,2-dimethyoxyethane, 3 mL of triethylamine, and 11 mL of chlorotrimethylsilane, was added to the cold solution (0 °C) of the lithium enolate. This solution was stirred for 15 min and was then partitioned between pentane and cold aqueous sodium bicarbonate. The organic layer was separated, dried with sodium sulfate, and then concentrated. Fractional distillation produced 4.2 g of the 6-methylcyclohex-1-enol trimethylsilyl ether, which was characterized by thin-layer chromatography, gas chromatography, and ^{1}H NMR. The ^{1}H NMR spectrum is consistent with that of the NMR reported by House et al.[12] The ratio of the 6-methyl- to the 2-methylcyclohex-1-enol trimethylsilyl ether isomers was determined to be at least 98:2.

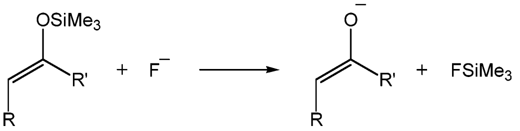
2-Methylcyclopent-1-enol trimethylsilyl ether (**II**) and 5-methylcyclopent-1-enol trimethylsilyl ether (**III**) were prepared simultaneously and then separated by preparatory gas chromatography. 2-Methylcyclopentanone (0.07 mol) was added to a solution of chlorotrimethylsilane (0.085 mol) and triethylamine (0.170 mol) in 30 mL of dimethylformamide. The mixture was refluxed for 4 h and then cooled and diluted with 60 mL of pentane. The resulting solution was washed in rapid succession with cold aqueous 1.5 M HCl and cold aqueous sodium bicarbonate. The organic layer was dried with magnesium sulfate, concentrated, and fractionally distilled. The structures were confirmed by ^{1}H NMR and agreed with the literature values.[12] The purities were >98% on the basis of the ^{1}H NMR spectra.

Ion Formation. A fluoride ion, the primary ion in our experiments, was produced by dissociative electron attachment to nitrogen trifluoride (eq 1). Some of the enolate anions, such as 4-methylcyclohex-1-enolate, were formed from ketones and were generated according to eq 2. In cases where the silyl enol ether was synthesized, the enolate anion was formed by an S_N2 reaction on the Si center,[13] according to eq 3. The cyclopent-1-enolate derivatives are shown in Figure 4, and the cyclohex-1-enolate derivatives are shown in Figure 5. The partial pressure of each neutral gas was about 1 × 10^{-7} to 2 × 10^{-7} Torr.

$$e^- + NF_3 \longrightarrow F^- + NF_2 \qquad (1)$$



(2)



(3)

Instrumentation. Ions were detected in a continuous wave ion cyclotron resonance (CW-ICR) mass spectrometer.[14] The cell, which has a 1-in. square cross section, was placed between the poles of an electromagnet, operated between 0.2 and 1.0 T. Background pressures were typically 5 × 10^{-9} Torr, and the operating pressure was typically about 2 × 10^{-7} to 4 × 10^{-7} Torr. At these pressures, average trapping times of the ions were on the order of 1 s. We estimate that the temperature in the cell was approximately 350 K.[15] A capacitance bridge with phase-sensitive amplification was employed to detect the oscillating potential on the cell's analyzer plate, induced by the motion of the ions.[16] Signal detection at the frequency corresponding to the maximum of the mass peak was accomplished with a frequency lock.[16] Changes in the steady-state ion population of as little as 0.5% were detectable.

The light source for the low-resolution photodetachment experiments was a Schoeffel 1000 W Xenon arc lamp. Wavelengths were selected by a 0.25 m focal length Spectral Energy monochromator with a visible grating (350−1100 nm). When we used 7.7 mm slits, the bandwidth was 25 nm (full width at half-maximum). The monochromator was calibrated using a Beck reversion spectroscope, accurate to about 1 nm. Relative power was measured by focusing the exit light from the monochromator into a thermopile (Eppley Laboratory, Inc.) and recording the output voltage. This was done immediately before or after an experimental run because the experimental setup precluded recording the power during the experiment.

The light source for the high-resolution electron photodetachment experiments was a Lexel tunable CW Ti/Sapphire laser, pumped by a Coherent model I-200 argon ion laser. Wavelength selection was accomplished by a three-plate birefringent filter mounted in the laser cavity. The bandwidth of the laser light was less than 40 GHz (about 1 cm^{-1}), and the wavelength reading, using a Beck reversion spectroscope, was accurate to about 1 nm (about 20 cm^{-1}). The relative power was measured by splitting off about 3% of the laser light and directing it into the thermopile during the experiment.

Data Acquisition. Electron photodetachment spectra were acquired by measuring the fractional decrease (FD, eq 4) of the steady-state signal of each enolate ion at each of several different wavelengths (λ). $I_{\text{on}}(\lambda)$ is the signal intensity with light,

$$\text{FD}(\lambda) = 1 - \frac{I_{\text{on}}(\lambda)}{I_{\text{off}}(\lambda)} \qquad (4)$$

and $I_{\text{off}}(\lambda)$ is the signal intensity without light. Relative cross sections, $\sigma(\lambda)$, were then calculated according to eq 5, where

$$\sigma(\lambda) \propto \frac{\text{FD}(\lambda)}{\lambda \cdot P(\lambda) \cdot [1 - \text{FD}(\lambda)]} \qquad (5)$$

$P(\lambda)$ is the relative power of the incident laser light.[14] For high-resolution spectra, data were taken about every 1 nm over regions of about 10−15 nm and the final spectra were constructed by splicing these overlapping regions together. For low-resolution spectra, data were taken about every 10 nm over regions of about 100 nm and the final spectra were obtained by splicing these overlapping regions together. In both cases, the overlapping regions typically overlapped for three data points.

Calculations

All calculations were performed using Gaussian 98.[17] The calculations were carried out at the UHF/6-31+G* level of theory. The vibrational frequencies reported are unscaled.

Results

We have recorded the low- and high-resolution electron photodetachment spectra of several enolates, anions, and enolate−anion mixtures. Deprotonation of 2-methylcyclopentanone results in two different enolate anions, 2-methylcyclopent-1-enolate and 5-methylcyclopent-1-enolate. The low- and high-resolution spectra are shown in Figure 6. The low-resolution spectrum has a photodetachment onset at 885 ± 20 nm. There are no visible slope changes. In the high-resolution spectrum, there is an onset at 877 ± 5 nm, a slope change at about 840 nm, and another at about 810 nm. There are no resonances visible.

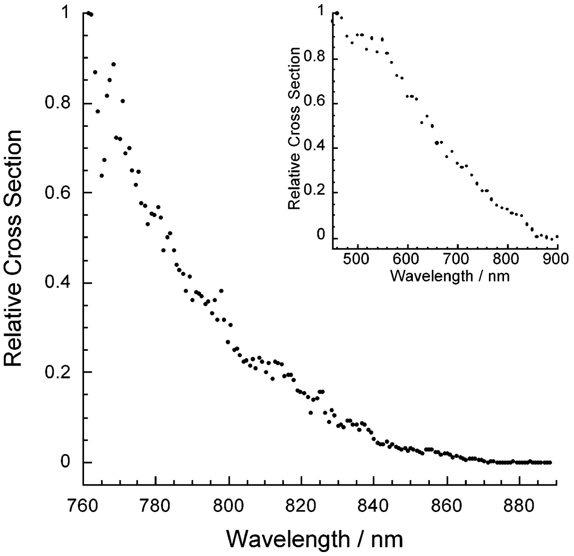


Figure 6. High-resolution spectrum, with the low-resolution inset, of a mixture of 2-methylcyclopent-1-enolate and 5-methylcyclopent-1-enolate from the deprotonation of 2-methylcyclopentanone.

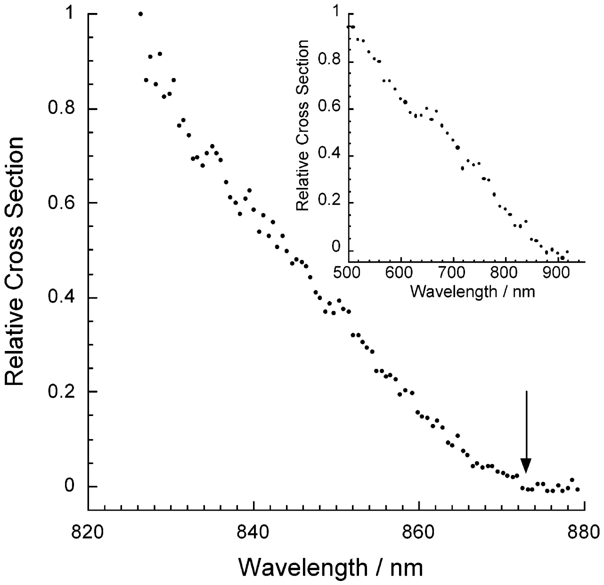


Figure 7. High-resolution spectrum of 2-methylcyclopent-1-enolate. The arrow indicates the assignment of the electron affinity. The low-resolution spectrum is shown as an inset.

In addition to taking the photodetachment spectra of the mixture of 2-methylcyclopent-1-enolate and 5-methylcyclopent-1-enolate, we have also taken the spectra of the individual species. The 2-methylcyclopent-1-enolate low-resolution spectrum, shown in Figure 7, has an onset for photodetachment at 880 nm. The high-resolution spectrum shows a nearly linear cross section with an onset at 873 nm. No slope changes or resonances are visible. The low-resolution photodetachment spectrum of the 5-methylcyclopent-1-enolate, shown in Figure 8, has an onset at 810 nm. The high-resolution spectrum shows a smoothly rising cross section with no discernible resonances.

The high-resolution photodetachment spectrum of the mixture of anions generated by the deprotonation of 3-methylcyclopen-

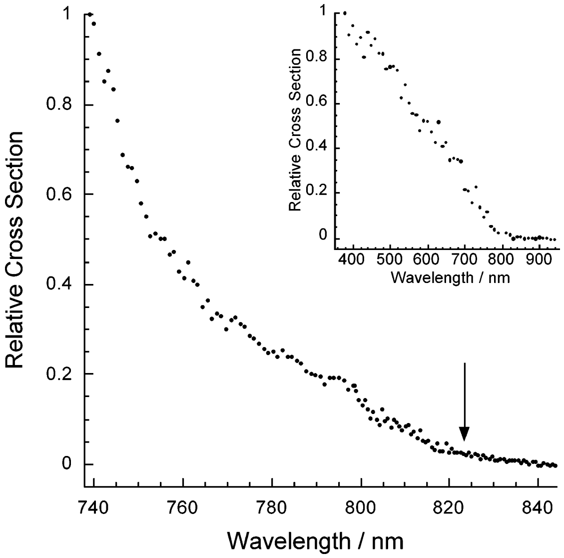


Figure 8. Low- and high-resolution spectrum of 5-methylcyclopent-1-enolate, with the low-resolution shown as an inset. The arrow indicates the assignment of the electron affinity.

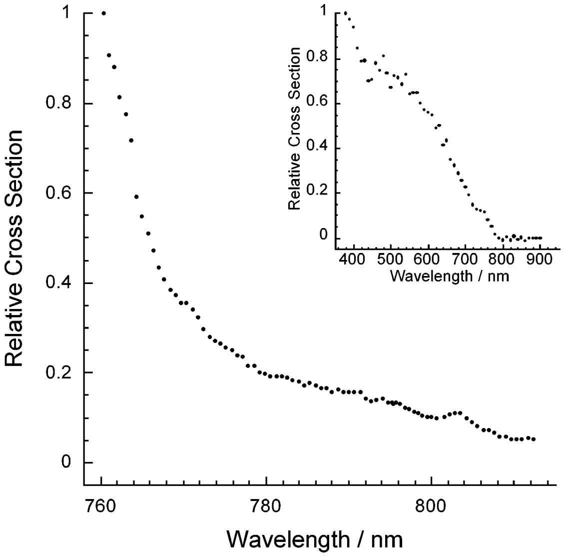


Figure 9. High-resolution photodetachment spectrum of 3-methylcyclopent-1-enolate and 4-methylcyclopent-1-enolate from the deprotonation of 3-methylcyclohexanone. The low-resolution spectrum is shown as an inset.

tanone is shown in Figure 9. A fairly smooth rising cross section can be observed. The low-resolution data show an onset at about 800 nm. Extrapolation of the highest-wavelength linear region in the high-resolution spectrum gives an onset at 820 nm. There is a slope change at about 780 nm. A small but reproducible dipole-bound state resonance is seen at 805 nm in the spectrum.

The low- and high-resolution photodetachment spectroscopy of 6-methylcyclohex-1-enolate is shown in Figure 10. The low-resolution spectrum is roughly linear for wavelengths shorter than 780 nm, and there is a slope change at about 780 nm. It is possible that a second linear region exists for wavelengths longer than 780 nm. However, there is a feature centered at about 820 nm in the low-resolution spectrum that obscures that region. The onset is seen at about 860 nm. In the high-resolution spectrum, there is a very broad resonance centered at 843 nm and the onset for photodetachment is at about 915 nm. In addition, there is a linear region for wavelengths shorter than 820 nm.

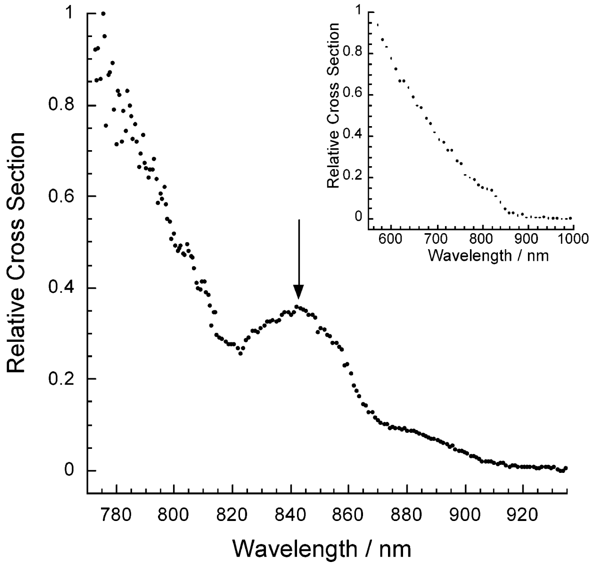


Figure 10. High-resolution photodetachment spectrum of 6-methylcyclohex-1-enolate, with the low-resolution spectrum as the inset. The arrow indicates the assignment of the electron affinity.

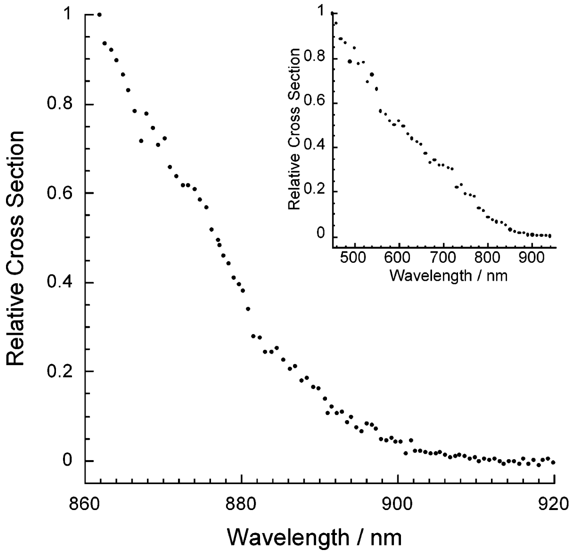


Figure 11. High-resolution spectrum of a mixture of 2-methylcyclohex-1-enolate and 6-methylcyclohex-1-enolate, with the low-resolution spectrum as an inset.

Deprotonation of 2-methylcyclohexanone results in two different enolate anions, 2-methylcyclohex-1-enolate and 6-methylcyclohex-1-enolate. The spectra of this mixture are shown in Figure 11. The low-resolution spectrum shows a gradually rising cross section. The onset is at about 905 nm. In the high-resolution spectrum, the threshold is 902 ± 5 nm. There is a slope change at 885 nm, and no resonances can be seen.

Deprotonation of 3-methylcyclohexanone results in two different enolate anions, 3-methylcyclohex-1-enolate and 5-methylcyclohex-1-enolate. In the high-resolution spectrum shown in Figure 12, the onset is at 826 ± 5 nm. There are no noticeable slope changes and no resonances visible.

The high-resolution spectrum of 4-methylcyclohex-1-enolate is shown in Figure 13 with the low-resolution spectrum as an inset. In the low-resolution data, there are three linear regions: one below 600 nm, one between 600 and 700 nm, and one above 700 nm. The photodetachment onset is at 820 nm. In the high-resolution spectrum, there are two sharp resonances at 774 and 788 nm.

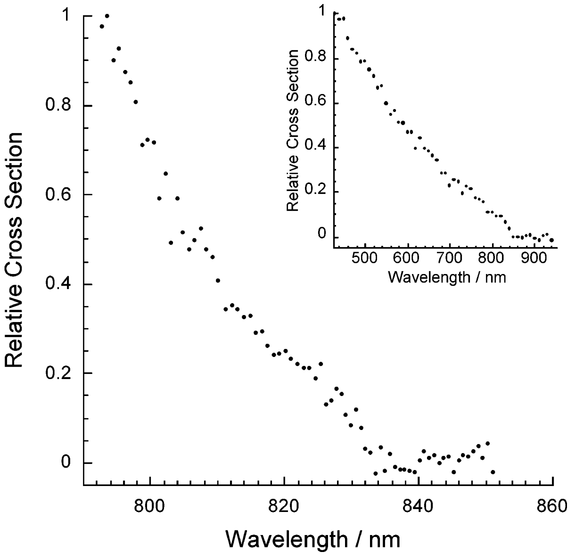


Figure 12. High-resolution spectrum of a mixture of 3-methylcyclohex-1-enolate and 5-methylcyclohex-1-enolate, with the low-resolution spectrum as an inset.

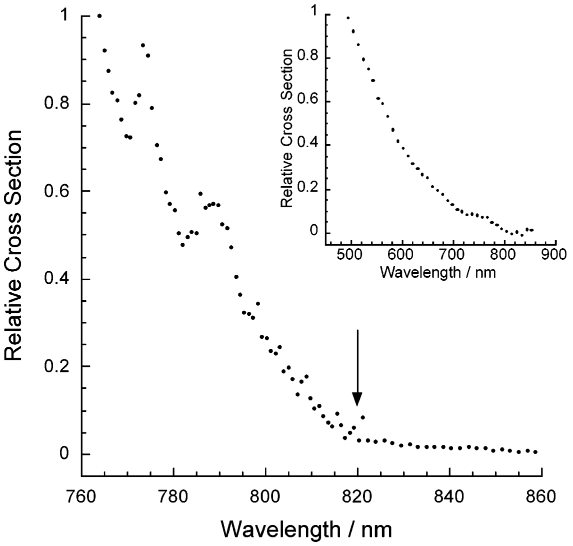


Figure 13. High-resolution spectrum of 4-methylcyclohex-1-enolate, with the low-resolution spectrum shown in the inset. The arrow indicates the assignment of the electron affinity.

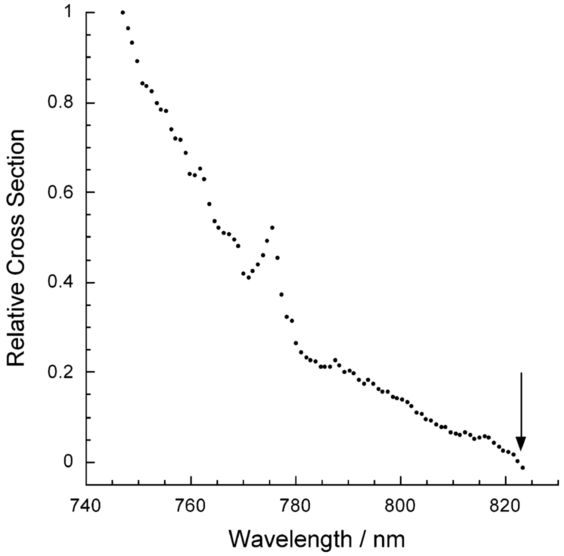


Figure 14. High-resolution spectrum of 4-ethylcyclohex-1-enolate. The arrow indicates the assignment of the electron affinity.

TABLE 1: Electron Affinities of the Enolate Radicals Studied

anion	electron affinity[a] (nm)	electron affinity[a] (kcal mol^{-1})
cyclopent-1-enolate[b]	775.8 ± 3	36.8 ± 0.2
2-methylcyclopent-1-enolate	873 ± 5	32.8 ± 0.2
3-methylcyclopent-1-enolate[c]	805 +5/−25	35.5 +1.1/−0.2
4-methylcyclopent-1-enolate[c]	805 +5/−25	35.5 +1.1/−0.2
5-methylcyclopent-1-enolate	823 ± 5	34.7 ± 0.2
cyclohex-1-enolate[b]	812.6 ± 5	35.2 ± 0.2
2-methylcyclohex-1-enolate[d]	902 ± 5	31.7 ± 0.2
3-methylcyclohex-1-enolate[e]	826 +5/−20	34.6 +0.9/−0.2
4-methylcyclohex-1-enolate	820 ± 2	34.9 ± 0.2
4-ethylcyclohex-1-enolate	823 ± 5	34.7 ± 0.2
5-methylcyclohex-1-enolate[e]	826 +5/−20	34.6 +0.9/−0.2
6-methylcyclohex-1-enolate	843 ± 10	33.9 ± 0.4
cyclohept-1-enolate[b]	858.6 +2/−13	33.3 +0.5/−0.1

[a] The electron affinity of the radical corresponding to photodetachment of the extra electron in the anion. [b] The cyclopentanone enolate anion, the cyclohexanone enolate anion, and the cycloheptanone enolate anion were published by Brinkman et al.[22] [c] Produced as a mixture of 3-methylcyclopent-1-enolate and 4-methylcyclopent-1-enolate. The large error bars reflect the uncertainty of assigning the mixture and were chosen to account for the possibility that one of them has a larger electron affinity (shorter wavelength). [d] Produced as a mixture of 2-methylcyclohex-1-enolate and 6-methylcyclohex-1-enolate. The electron affinity was assigned with certainty by knowing the electron affinity of the 6-methylcyclohex-1-enolate radical. [e] Produced as a mixture of 3-methylcyclohex-1-enolate and 5-methylcyclohex-1-enolate. The large error bars reflect the uncertainty of assigning the mixture and were chosen to account for the possibility that one of them has a larger electron affinity (shorter wavelength).

The high-resolution spectrum of 4-methylcyclohex-1-enolate is shown in Figure 13 with the low-resolution spectrum as an inset. In the low-resolution data, there are three linear regions: one below 600 nm, one between 600 and 700 nm, and one above 700 nm. The photodetachment onset is at 820 nm. In the high-resolution spectrum, there are two sharp resonances at 774 and 788 nm.

The high-resolution spectrum of 4-ethylcyclohex-1-enolate is presented in Figure 14. The onset is at about 823 nm, and there is a sharp resonance at 776 nm. There are two linear regions in the spectrum, one region for wavelengths below the peak and another region between the onset and the peak.

Discussion

Electron Affinity Assignment. To assign electron affinities of the radicals corresponding to photodetachment of the enolate anions we studied, we must determine the energy of the transition from the anions to the radicals in their ground electronic, rotational, and vibrational states. The electron affinities of these radicals are tabulated in Table 1. In the absence of other states, such as dipole-bound states, the intensity of the transition is determined by the Franck−Condon overlap between the anion and the radical. If the Franck−Condon overlap for the 0-0 transition between the anion and the radical is large enough, then the lowest-energy transition seen in the spectrum, in the absence of hot bands, will correspond to the adiabatic electron affinity. However, if the Franck−Condon overlap is too small, then the 0-0 transition will not be visible and we will overestimate the adiabatic electron affinity. From other studies on enolate anions,[8,18−22] we believe that the Franck−Condon overlap is large enough that the onset for photodetachment will correspond to the 0-0 transition and therefore will correspond to the adiabatic electron affinity. An additional concern is that the anion formed could be vibrationally excited. This would result in hot bands that would result in an underestimate of the adiabatic electron affinity. Because the ions are trapped for 100−1000 ms, they usually have enough time to relax by radiative and collisional processes, although hot bands are seen in some species.

The electron affinity is assigned by analyzing the low- and high-resolution spectra simultaneously. Because the ions are trapped and allowed to relax, we expect most of the anions formed to be in the ground vibrational state, although we do expect that some will be in excited vibrational states. Species in excited vibrational states can give rise to hot bands in the spectra if the Franck−Condon overlap is sufficiently large. Because most of the anions are in the ground vibrational state, at energies above the threshold, the photodetachment spectrum will be dominated by 0-0 transitions rather than by hot bands. Even if a few of the predicted low-energy modes of these anions were populated, these only appear in the spectrum energetically below the threshold by the amount of energy of that vibrational state. Although higher-energy vibrations would appear much lower in energy in the spectrum than in the adiabatic electron affinity, these states become increasingly less-populated the higher in energy they are. By extrapolating a section of the low-energy portion of a low-resolution spectrum to zero cross section, we feel confident that we can distinguish hot bands from cold bands and that we can obtain a good estimate of the adiabatic electron affinity.

In the absence of threshold peaks in the high-resolution data, the extrapolation to zero cross section of the low-resolution spectrum is taken as the adiabatic electron affinity. When there are threshold peaks in the high-resolution data, they are used to help assign the electron affinity. From previous work in this laboratory on similar species, we believe that the peaks seen in these spectra are dipole-bound states and that they are bound by only 5−10 cm^{-1}.[9] Because they are bound so weakly, the lowest-energy peak corresponds to transition to the ground vibrational state but an excited rotational state. The excited electron is so weakly bound that only a few quanta of rotational energy for the molecule is sufficient to make the total energy enough to detach the electron.[23] Therefore, a peak at the threshold is the unresolved envelope of the P, Q, and R branches for the transition to the ground vibrational state of the excited electronic state. The intensity of the P and R branches will be lowered slightly because some of the product states are still bound, but by taking the center of the envelope as the $\Delta J = 0$ transition, we can make a good approximation of the adiabatic electron affinity.

The electron affinity of a radical is the difference between the energy of the anion (formed by adding an electron to the radical) and the energy of the radical. For stable anions, such as the enolate anions in this study, this value is positive. To a first approximation, we expect all of these species to have similar electron affinities because their structures and energetics are so similar. For example, all of the radicals should have similar dipole moments and polarizabilities. However, because the species are chemically different, we do expect small differences in the electron affinity on the order of a few kilocalories per mole.

Deprotonation of 2-methylcyclopentanone gives two anions, 2-methylcyclopent-1-enolate and 5-methylcyclopent-1-enolate. The low-resolution spectrum has an onset at 885 nm. The high-resolution spectrum has an onset at 877 nm. Zimmerman noted that methyl substitution for a hydrogen at the site of deprotonation lowers the electron affinity considerably.[21] Therefore, we tentatively assign the onset of photodetachment as the electron affinity of the 2-methylcyclopent-1-enolate radical. Although we considered assigning the slope change at 840 nm as the electron affinity of the 5-methylcyclopent-1-enolate radical, this cannot be done without more conclusive evidence.

The high-resolution photodetachment spectrum of 2-methylcyclopent-1-enolate displays a fairly sharp onset at 873 ± 5 nm. The electron affinity for the 2-methylcyclopent-1-enolate radical is assigned at the onset and has a value of 32.8 ± 0.2 kcal/mol (1.42 ± 0.009 eV). This is very close to the electron affinity that was tentatively assigned by analyzing the mixture of the above species.

An extrapolation of the low-resolution photodetachment spectrum of 5-methylcyclopent-1-enolate gives an onset at about 820 nm. The high-resolution photodetachment spectrum of 5-methylcyclopent-1-enolate has an onset at 837 ± 5 nm. The discrepancy between this onset and the one seen in the low-resolution spectrum is attributed to hot bands. A linear extrapolation of the high-resolution region between 770 and 815 nm gives an onset at 823 ± 5 nm, which is consistent with the low-resolution spectrum. The electron affinity for the corresponding radical is assigned at this value. The cross section at wavelengths shorter than that of the slope change is a combination of the cross sections of the 2- and 5-methylcyclopent-1-enolate. The electron affinity of the 5-methylcyclopent-1-enolate radical is assigned as 34.7 ± 0.2 kcal/mol (1.506 ± 0.009 eV).

Deprotonation of 3-methylcyclopentanone gives two products, 3-methylcyclopent-1-enolate and 4-methylcyclopent-1-enolate. The high-resolution spectrum of this mixture has a dipole-bound state resonance at 805 nm. The assignment of the electron affinity at this dipole-bound state resonance is consistent with the low-resolution data, which show an onset at about 800 nm. It is unclear which isomer this dipole-bound state and electron affinity correspond to, but both of them are probably very similar in electron affinity and probably have similar dipole-bound states. It is possible to assign the same electron affinity to both of them if sufficiently large error bars are used. The error bars chosen are large enough to incorporate the slope change at 780 nm. Using an onset of 805 +5/−25 nm, we get electron affinities of 35.5 +1.1/−0.2 kcal/mol (1.54 +0.05/−0.01 eV).

We can assign the electron affinity of the 6-methylcyclohex-1-enolate radical by analyzing the low- and high-resolution photodetachment spectra. Extrapolation of the short wavelength linear region in the low-resolution spectrum between 630 and 780 nm gives an onset at 830 ± 13 nm. Extrapolation of the wavelength region longer than 780 nm in the low-resolution spectrum is difficult because of the feature centered at about 820 nm. However, extrapolation of that region gives an onset estimation at about 860 nm. On the basis of these two extrapolations of the low-resolution spectrum, we expect the electron affinity to lie somewhere between 830 and 860 nm. Therefore, in the high-resolution spectrum, we attribute the nonzero cross section at wavelengths longer than 860 nm to hot bands. We believe that the peak centered at 843 nm in the high-resolution spectrum is a dipole-bound state resonance at the threshold. Although this peak is considerably broader than a typical dipole-bound state peak, we believe that this is a dipole-bound state that is considerably lifetime broadened. In addition, the extrapolation of the wavelength region shorter than 820 nm in the high-resolution spectrum gives an onset at 835 nm. On the basis of this extrapolation and the position of the resonance, we assign the center of the dipole-bound state resonance as the electron affinity. Because of the width of this peak, we assign larger error bars to accompany this assignment. Therefore, we assign the electron affinity of the 6-methylcyclohex-1-enolate radical at 843 ± 10 nm (33.9 ± 0.4 kcal/mol; 1.470 ± 0.02 eV).

Deprotonation of 2-methylcyclohexanone gives two products, 2-methylcyclohex-1-enolate and 6-methylcyclohex-1-enolate. Both the low- and the high-resolution photodetachment spectra of this mixture have a threshold at about 902 nm. Because the 6-methylcyclohex-1-enolate radical was assigned an electron affinity at 843 nm, the threshold at 902 nm in the high-resolution spectrum of the mixture must be the threshold for detachment of 2-methylcyclohex-1-enolate. We therefore assign the electron affinity of the 2-methylcyclohex-1-enolate radical at 902 ± 5 nm, which corresponds to 31.7 ± 0.2 kcal/mol (1.375 ± 0.009 eV).

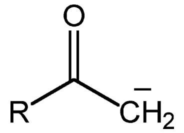
Deprotonation of 3-methylcyclohexanone gives two products, 3-methylcyclohex-1-enolate and 5-methylcyclohex-1-enolate. The high-resolution spectrum of this mixture has an onset for photodetachment at 826 ± 5 nm, which is consistent with the low-resolution photodetachment onset at 840 nm. It is unclear which species this corresponds to, but both of them are probably very similar. It is possible to assign both of their electron affinities if sufficiently large error bars are used. Using an onset of 826 +5/−20 nm, we get electron affinities of 34.6 +0.9/−0.2 kcal/mol (1.501 +0.04/−0.009 eV).

Extrapolation of the linear region above 700 nm in the low-resolution spectrum of 4-methylcyclohex-1-enolate gives an onset at 810 ± 13 nm. The two sharp resonances in the high-resolution spectrum of 4-methylcyclohex-1-enolate are dipole-bound states. Although the electron affinity is usually assigned as the lowest-energy dipole-bound state, in this case, we did not do that. The dipole-bound state at 788 nm is far above the photodetachment threshold, which is not the typical case for dipole-bound states of enolate anions. In addition, assignment of the electron affinity at 788 nm would be inconsistent with the low-resolution data, which suggests an electron affinity at about 810 nm. Extrapolation of the linear region in the high-resolution spectrum gives an onset at 820 ± 5 nm, which we assign as the electron affinity. This corresponds to 34.9 ± 0.2 kcal/mol (1.512 ± 0.009 eV). We believe that the dipole-bound states seen in this spectrum are vibrationally excited.[24]

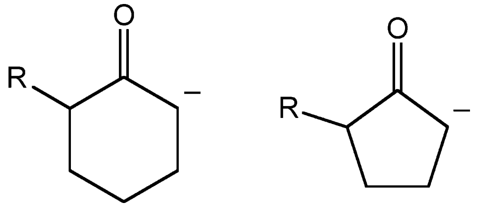
The high-resolution spectrum of 4-ethylcyclohex-1-enolate shows a resonance at 776 nm. Normally, the electron affinity would be assigned at this peak. However, the electron affinity is not assigned here because this dipole-bound state is significantly above the photodetachment threshold. In addition, an assignment at the dipole-bound state would be considerably higher in energy than the electron affinity of the corresponding radical of 4-methylcyclohex-1-enolate. Because the additional methylene group only stabilizes the anion by polarizability effects, there is no reason to believe that the difference in electron affinities would be so large on the basis of the distance between the methylene group and the charge center. Instead, we assign the electron affinity as the photodetachment onset at 823 ± 5 nm, which corresponds to 34.7 ± 0.2 kcal/mol (1.506 ± 0.009 eV).

Methyl Substitution. Zimmerman et al. studied a series of small acyclic enolate anions and analyzed some of the trends of the effects that substituents have on electron affinities.[21] They noted that increasing the size of alkyl groups that are away from the charge center increases the electron affinity. They analyzed substitution effects on the series shown in Scheme 1, where R = Me, Et, and *t*-Bu. They found that R = H had a higher electron affinity than R = Me or Et, which was rationalized by considering that alkyl groups are electron donating when bonded to unsaturated carbons. The effect is in competition with the polarizability, which increases as the size of the species increases. Indeed, they discovered that the R = methyl and R = ethyl species have nearly the same electron affinity. Then, as the size of the group increases, the polarization also increases, which stabilizes the anion, increasing the electron affinity. For the R = *t*-Bu species, the electron affinity increase is larger than that for even the R = H species.

SCHEME 1: Enolate Anions with Substitution on the Carbon Opposite to the Charged Carbon



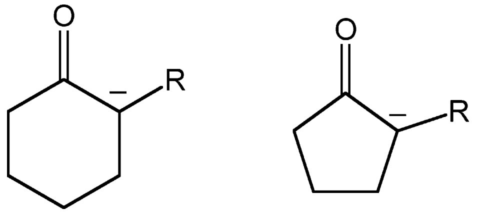
SCHEME 2: Substitution of Cyclic Enolate Anions at the Carbon Opposite to the Charge



In this study, we find that alkyl substitution away from the charge center does not increase the electron affinity and, in fact, decreases it slightly. We studied the species in Scheme 2, where R = H and Me. For our enolates, R = H is similar to Zimmerman's R = Me and our R = Me is similar to Zimmerman's R = Et. (We do not have an example similar to that of Zimmerman's R = *t*-Bu, and we did not test the effect of alkyl group size other than at the 4-position. The effects in that case are too small to be considered significant.) In both the six- and five-membered cyclic enolate species, methyl substitution results in a less positive electron affinity. There is a 1.3 kcal/mol difference between the electron affinities for R = H and R = Me in the six-membered ring and a 2.1 kcal/mol difference for the five-membered ring. The effect is in the same direction when alkyl groups are substituted for hydrogens on any position in the ring. For the five-membered ring, the effect is smallest when the methyl group is farthest from the charge site. For the six-membered ring, the effect was about the same for the 3-, 4-, and 5-positions. Although we expect that the anion should be stabilized because of the larger polarization when an alkyl group is substituted for a hydrogen, the effect is smaller for our species than for that of Zimmerman's because our molecules are so much larger. For carbons near the site of unsaturation, substitution destabilizes the anion more than the increased polarization stabilizes it, resulting in a decreased electron affinity.

Zimmerman also looked at the effects of substitution at the site of deprotonation. Substitution of a methyl group for a hydrogen on the charged carbon makes the electron affinity less positive because the methyl group is electron donating when bonded to unsaturated carbons.[25,26] This destabilizes the anion, resulting in a smaller electron affinity. They reported a 2.8 kcal/mol difference between the electron affinities of acetaldehyde and propionaldehyde. We see the same trend in electron affinity when the cyclic enolates are methyl-substituted at the 2-position. Our results are more dramatic: 3.5 and 4.0 kcal/mol for the six- and five- membered rings, Scheme 3. Again, alkylation destabilizes the anion through electron donation but stabilizes it through the increased polarization. The increased polarization

SCHEME 3: Substitution at the 2-Position of the Cyclic Enolate Anions



is smaller for our species because our molecules are much larger than those reported by Zimmerman.

4-Methylcyclohex-1-enolate and 4-Ethylcyclohex-1-enolate. The comparison between these two spectra provides additional insight into these two species. Within experimental error, they have the same electron affinities, and both species have a resonance at about 775 nm, which is about 46 nm above the threshold. The 4-methylcyclohex-1-enolate has an additional resonance at 788 nm. An overlay of the two species is shown in Figure 15. Because these resonances are above the threshold, they are transitions to vibrationally excited dipole-bound states. There are several mechanisms through which these vibrationally excited species can autodetach: rotational−electronic, vibrational−electronic, and vibrational−rotational−electronic. The vibrational−electronic coupling should be similar for the two species, so any differences should come from vibrational−rotational−electronic couplings.

Because the weakly bound electron in a dipole-bound state is very far away from the core, the core geometry closely resembles the geometry of the neutral radical. The most significant geometry changes between the anion and the radical are in the C−O distance and in the C−C−O bond angle. Therefore, vibrational modes with changes in these parameters are expected to be the most active.

The two dipole-bound state resonances at 774 nm are nearly the same energy above the threshold, and they have the same width and size relative to the rising background. Therefore, it is likely that they are transitions to similar vibrational states. The vibrational energy of the dipole-bound state at 774 nm is about 730 cm^{-1}. Calculations of the vibrational modes of the radicals reveal a vibration at about 715 cm^{-1} that has a large change in the C−C−O angle. In this vibrational mode, the distance between the cyclohexenolate ring and the alkyl substituent also changes, although there are no rotations or torsions of the alkyl group. Because these two resonances have the same half-width, it is clear that the two states have about the same lifetimes. The substitution of ethyl for methyl does not decrease the lifetime of the species by coupling to electronic or rotational states.

The resonance that appears at 788 nm in the spectrum of 4-methylcyclohex-1-enolate does not appear in the spectrum of 4-ethylcyclohex-1-enolate. This resonance corresponds to a vibrational energy of about 470 cm^{-1}. The 4-methylcyclohex-1-enolate radical is calculated to have two vibrations in this region that are expected to be active, one at 434 cm^{-1} and one at 467 cm^{-1}. Both of them have a significant rocking of the methyl group that accompanies the C−C−O bend. Because this dipole-bound state is broader than the one at 774 nm, it is likely that this mode couples to the electronic or rotational motion of the molecule, reducing the lifetime of the species. The 4-ethylcyclohex-1-enolate radical also is calculated to have two modes in this region with significant C−C−O bends, one at 429 cm^{-1} and one at 466 cm^{-1}. Both of these modes have significant torsional motion of the ethyl group. Because of the similarity between the 4-methyl and 4-ethyl species, it is possible that one or both of these vibrationally excited dipole-bound states are accessed in the photodetachment process; however, the twisting of the ethyl group couples to the rotational motion, and the lifetime of the species is shortened, which lifetime broadens the peak. This highlights an important aspect of the photodetachment spectra presented here. Although the species that have observable dipole-bound states are calculated to have vibrations that energetically could be seen in our high-resolution photodetachment spectra, their absence could be a result of coupling similar the coupling of the 4-ethyl species or could simply be the result of a poor Franck−Condon overlap integral between the ground state anion and the vibrationally excited dipole-bound state.

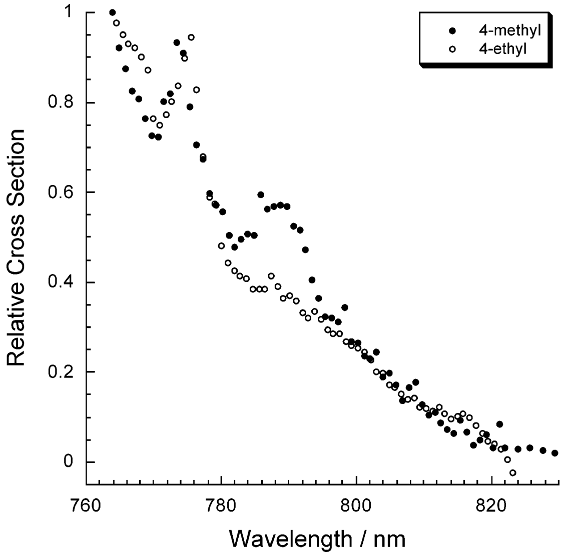


Figure 15. Overlay of 4-methylcyclohex-1-enolate and 4-ethylcyclohex-1-enolate high-resolution spectra.

Summary

We have used high- and low-resolution photodetachment spectroscopy to measure the electron affinities for a series of alkylated cyclic enolate radicals. The effects of alkylation at various positions are examined. The size of the effect did not have much effect on the electron affinity, but it was shown to have a dramatic effect on the lifetimes of dipole-bound states in the case of 4-methylcyclohex-1-enolate and 4-ethylcyclohex-1-enolate.

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