

Electron Photodetachment from Cyclic Enolate Anions in the Gas Phase: Electron Affinities of Cyclic Enolate Radicals

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Abstract: Relative electron photodetachment cross sections have been measured for a number of cyclic enolate anions, using an ion cyclotron resonance spectrometer to trap and detect the ions. The electron affinities of the neutral radicals are determined for enolate systems derived from cyclic ketones having four- through twelve-membered rings. The observed trend in electron affinities is correlated with the geometries of the enolates. The estimated electron affinities for the respective enolate radicals are (kcal/mol): cyclobutanone (42.5 ± 1.5), cyclopentanone (37.3 ± 1.3), cyclohexanone (35.8 ± 1.2), cycloheptanone (34.2 ± 1.0), cyclooctanone (37.6 ± 1.3), cyclononanone (39.0 ± 1.4), cyclodecanone (42.3 ± 1.5), cyclododecanone (43.9 ± 1.7), 2-norbornanone (37.1 ± 1.2), and 2,5-dimethylcyclopentanone (34.4 ± 1.0).

Electron photodetachment threshold measurements have become an important method for obtaining electron affinities of molecular systems.¹⁻⁴ Besides having significant thermochemical value, electron affinities are important because they reflect the intrinsic stability of a negative ion relative to the corresponding neutral. Considerable interest has centered around using electron affinities to investigate the effects of substituents on negative ion stabilities,³⁻⁵ thereby obtaining information concerning the electronic structures of the anions and the corresponding neutrals. In studies of this type, however, it is often difficult to distinguish geometrical or hybridization effects from those due to electron delocalization or dipolar interactions with the substituent.

This situation suggested the need to study the effects of varying geometrical constraints on anion stabilities, while keeping resonance and dipolar interactions essentially constant. In this report we address this problem by determining electron affinities and examining the stabilities of a series of enolate anions derived from cyclic ketones, $(\text{CH}_2)_n\text{CO}$, $3 \leq n \leq 11$. Because of increasing polarizability of the larger alkyl chains, we expect a gradual increase in electron binding energy in this series as the molecular size is increased.⁴ Any pronounced deviations from this expected trend in anion stabilities may then be attributed to changing interactions as the geometrical constraint of ring strain is relaxed.

Experimental Section

All negative ions were generated and trapped in a modified V-5900 ion cyclotron resonance spectrometer¹ using cell plate potentials similar to those previously described.⁵ Cell pressures were about 10^{-6} Torr, allowing ions to be trapped for about 1 s. In all cases the enolate anions were generated by using F^- to abstract an acidic proton from the α carbon of the parent ketone. The F^- was formed from NF_3 by dissociative electron impact at 1.7 eV (electron energy minus trapping voltage). All of the ketones used were from Aldrich Chemical Co. except cyclopentanone and cyclohexanone (MCB); all of the ketones were used without additional purification.

The light source used for the photodetachment experiments consisted of a 1000-W xenon arc lamp used in conjunction with a grating monochromator. The spectral bandwidth of the monochromator was 23.8 nm (fwhm) for all experiments. Maximum photodestruction of the enolate anions varied from 5–17% depending on the anion. The method of data collection and analysis has been previously described.^{1a}

Results

We have measured photodetachment cross sections as a function of photon wavelength for enolate anions derived from cyclobutanone, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, 2,5-dimethylcyclopentanone, cyclono-

nanone, 2-norbornanone, cyclodecanone, and cyclododecanone. Representative cross sections, shown in Figure 1 for cyclobutanone and cyclopentanone enolate anions, closely resemble in overall appearance the cross sections for the other cyclic enolates as well as those which we have investigated previously for the corresponding noncyclic enolate anions.⁵ Each cross section rises more or less linearly from threshold, then tends to level off somewhat at shorter wavelengths. This behavior suggests an interpretation similar to that which we previously made for the noncyclic enolate anions.⁵ That is, these ions look like slightly perturbed allyl systems.

We expect that each cyclic enolate anion cross section is composed of a superposition of a number of vibronic transition cross sections, each vibronic onset being relatively sharp from symmetry considerations.⁶ After a sudden onset each vibronic partial cross section shows a more slowly rising region at higher photon energies. A number of off-diagonal Franck-Condon transitions are expected to be observed, but geometry changes are not expected to be so severe as to shift all intensity from the diagonal transitions. This assumption is consistent with the tendency of the experimental cross sections to level off at high photon energies. The vibrational hot-band intensities are expected to be weak except for transitions from low-lying vibrational levels with relatively high thermal populations, which will occur quite near the 0-0 transition. Therefore we expect to introduce little error in determining thresholds by neglecting the hot bands.⁷ Estimates for the electron affinities of the enolate radicals are obtained by subtracting the spectral bandwidth from the observed thresholds. These electron affinities are tabulated in Table I as EA, the uncertainties corresponding to the spectral bandwidth of the monochromator, 23.8 nm. The EA values in Table I correspond to adiabatic electron affinities if our assumptions about the extent of hot bands and off-diagonal vibronic transition intensities are valid in these systems. The error limits are fairly conservative, and it is quite likely that the differences between compounds are more reliable than the absolute values.

Discussion

The electron affinities in Table I reflect the changes in anion stability which occur as the cyclic system is increased in size. In Figure 2 the electron affinities are plotted as a function of the number of carbon atoms in the cyclic system. In the absence of geometric constraints a gradual increase in electron affinity with number of atoms is expected,⁴ a trend which is observed to some extent for cyclic systems with more than seven carbon atoms. However, a striking increase in electron affinities occurs for the smaller cyclic enolate systems, resulting in an electron

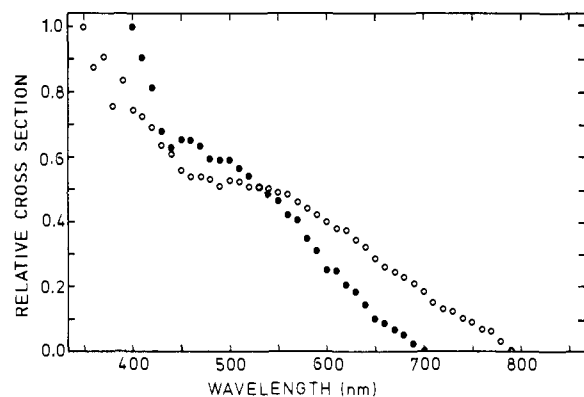


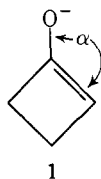
Figure 1. Relative photodetachment cross sections for enolate anions generated from cyclobutanone (●) and cyclopentanone (○). Maximum fractional decreases in the anion signals were 0.05 and 0.10, respectively.

affinity for cyclobutanone enolate which is almost as great as that for cyclododecanone enolate.⁸ This increasing stability for small ring enolate anions cannot be due to resonance or dipolar interactions but is likely to result from bonding changes associated with increasing ring strain.

It is well known that the acidities of carbon acids increase with increasing *s* character in C–H bonds; thus, the solution acidity order acetylene > ethylene > ethane is observed along with the relatively high acidity of molecules such as cyclopropane. This increased acidity can be understood by noting that the resulting anion has its unshared electrons in an orbital containing substantial *s* character. A simple perturbation model which we have described earlier⁹ is applicable to this situation and correctly predicts both an increased C–H bond strength as well as increased acidity. This model would also predict the electron affinities of localized small-ring radicals to be large. However, in the case of enolate anions, this analysis is not appropriate, because the carbon is rehybridized to allow the electron pair to be delocalized onto the carbonyl group. The electrons are forced to be in an orbital with *p* symmetry which overlaps with the carbonyl π bond. Because the electrons in both the radical and the anion are delocalized, one might expect little, if any, hybridization effect.

A plausible origin of the effect of ring size on cyclic enolate electron affinities is the interaction between the ends of the O–C–C π system. This interaction is attractive for an enolate or allyl cation and repulsive for the respective anions but less repulsive for the radicals. This gives rise to the CCC bond angle trend predicted by Boerth and Streitwieser for the allyl system: cation < radical < anion.¹⁰ Similarly, in the enolate system we calculated⁵ $\alpha(\text{OCC}) = 123^\circ$ for the radical and $\alpha(\text{OCC}) = 132^\circ$ for the anion ($\alpha = \text{OCC}$ angle).

For the cyclobutanone enolate anion, the angle α , shown in 1 is constrained to be about 135° . Since the O–C–C overlap



is nearly optimized at this angle we would expect this anion to be particularly stable, giving rise to the large electron affinity of the cyclobutanone enolate radical. For the five- and six-membered ring system, $\alpha \approx 126^\circ$ and 120° , respectively, and we expect the enolate anions for these cases to be destabilized (smaller electron affinity for the neutrals) due to the smaller OCC angle. For the cycloheptanone enolate anion, we expect the ring to distort in such a way as to increase the OCC angle

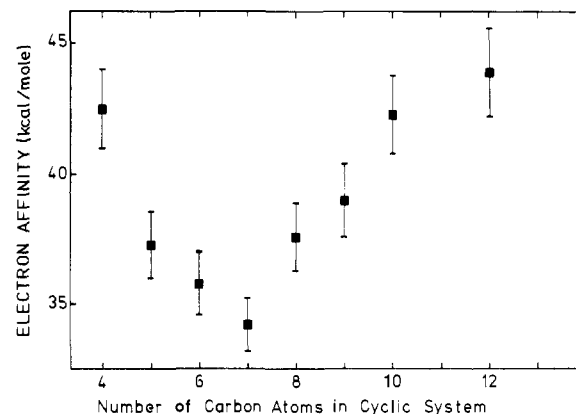


Figure 2. Electron affinities of enolate radicals as a function of the number of carbon atoms in the cyclic system.

Table I. Photodetachment Thresholds and Electron Affinities in Cyclic Enolate Systems

parent ketone	threshold, nm	EA, kcal/mol
cyclobutanone	698	42.5 ± 1.5
cyclopentanone	790	37.3 ± 1.3
cyclohexanone	822	35.8 ± 1.2
cycloheptanone	860	34.2 ± 1.0
cyclooctanone	784	37.6 ± 1.3
cyclononanone	757	39.0 ± 1.4
cyclodecanone	700	42.3 ± 1.5
cyclododecanone	675	43.9 ± 1.7
2-norbornanone	795	37.1 ± 1.2
2,5-dimethyl-cyclopentanone	856	34.4 ± 1.0

from the constrained value of 116° . However, the electron affinity of the cycloheptanone enolate radical is lower than that for the six-membered ring indicating little release from geometrical constraint. Also, the electron affinity of the acyclic seven-carbon enolate radical (enolate of 4-heptanone) is 5.5 kcal/mol *larger* than the cyclic enolate⁵ giving further evidence that the seven-membered ring is still subject to the geometrical constraints responsible for the electron affinities of the smaller rings. It appears that for cyclic enolates with eight or more carbon atoms, the O–C–C system is not greatly affected by geometrical constraint and the electron affinity simply increases with the size (and polarizability) of the molecule. This polarizability effect should be present in the entire series, so that the observed minimum is not as deep as one might expect simply from the strain consideration.

The kinetic acidity of cyclic ketones in solution has previously been shown by Schriesheim and co-workers¹¹ to follow the same order as our electron affinity trend, with cyclobutanone substantially more acidic than cyclohexanone or an acyclic enolate. It was suggested that the stabilizing π overlap with the carbonyl group might be more difficult to obtain in the cyclohexanone system than in the other enolates due to strain. However, it is difficult to see how this model could predict that cyclobutanone is a stronger acid than an acyclic system. Thus, we believe our allylic overlap argument offers the correct explanation for the observed electron affinity trend.

While we expect that very large cyclic enolate anions should be stabilized by the increased polarizability of the alkyl system, we should also consider the possibility that some of the observed stabilization might be due to an internal solvation of the anion by the floppy alkyl system. To investigate the effects of alkyl groups constrained to lie near the enolate system, we have measured the electron affinities of the enolate radicals of 2-norbornanone and 2,5-dimethylcyclopentanone. No unex-

pected stability changes are observed for these anions. For 2-norbornanone the stability lies between that for five- and six-membered cyclic enolate anions. The enolate anion of 2,5-dimethylcyclopentanone shows a decrease in stability over cyclopentanone which is of the magnitude expected in going from a secondary to a tertiary system.⁵ These observations give no indication that through space internal solvation interactions are significant for these anions, although it is not clear that these two systems have the size or molecular flexibility to exhibit such interactions. The entire problem of internal solvation in negative ions remains to be explored more thoroughly.

Conclusions

Electron affinities for cyclic enolate radicals determined from photodetachment threshold measurements prove to be extremely sensitive to the interactions accompanying the imposition of geometrical constraint on the molecular system. From the observed electron affinity trend we conclude that angle strain is the major factor which determines the relative stabilities for the smaller cyclic enolate anions.

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The Water Content of a Micelle Interior. The Fjord vs. Reef Models

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Abstract: Water penetrates micelles up to at least the first seven carbons beyond which there exists a nonpolar core. Neither the recently proposed "fjord model" nor the "reef model" satisfactorily explains our data.

Forty years have passed since Hess reported the first X-ray diffraction patterns of soap micelles.¹ Yet micellar structure remains poorly understood even on the elementary level. Consider the uncertainty in the water concentration inside a micelle (i.e., the depth to which water penetrates into the hydrocarbon portion of the aggregates). Svens and Rosenholm in 1973 presented evidence that water permeates nearly to the center of the micelles.² At the other extreme, Stigter in 1974 stated that water at the micelle surface meets a nonaqueous core at an abrupt interface; the surfactant methylenes α to the ionic head groups lie within this core.³ We designate these two descriptions the "fjord" and the "reef" models (Figure 1). In an effort to differentiate the two hydration schemes, we have studied the ¹³C NMR of carbonyl groups inserted into micelles. Carbonyls were selected for the purpose because: (a) it is known that ¹³C chemical shifts of carbonyls are solvent sensitive⁴ and (b) carbonyls should perturb the micelle structure much less than fluorescent compounds,⁵ spin labels,⁶ and other environmental probes commonly used with micelles.

There are two ways to incorporate a carbonyl into a micelle. The carbonyl can be attached to an additive adsorbed inside a micelle (e.g., octanal in hexadecyltrimethylammonium bromide) or the surfactant itself can bear the carbonyl (e.g., 8-ketohexadecyltrimethylammonium bromide). Both approaches were exploited in the present work.

Experimental Section

¹³C NMR spectra were obtained with a Varian CFT-20 spectrometer. Typically, 100 000 transients were collected using 8-mm sample tubes bearing a coaxial inner cell with 10% dioxane in D₂O. The latter served for external referencing and locking purposes. Solvents were either reagent grade (methanol, 2-propanol), Spectro grade (acetonitrile, *n*-heptane), or distilled immediately prior to use (dioxane). 8-Ketohexadecyltrimethylammonium bromide (7-KHTAB), generously given to us by Professor R. Hautala, possessed satisfactory spectral and analytical properties. Hexadecyltrimethylammonium bromide was commercial material recrystallized from aqueous acetone. Specific sample concentrations and conditions are listed in Table I.

Chemical shifts of the dioxane reference (measured over a few days at constant transmitter offset) showed little variation with the solvent surrounding the inner cell: water (63.16), methanol (63.11), ethanol (63.11), acetonitrile (63.10), dioxane (62.96), and heptane (63.12).

Results and Discussion

In Table I we list ¹³C chemical shifts δ (relative to external dioxane) for several aldehyde and ketone carbonyls as a function of a solvent polarity parameter, E_T .⁷ Chemical shift values for acetaldehyde (column 3) increase by a sizable 12.6 ppm as the solvent changes from heptane to water. Figure 2A, based on the data in column 3, shows that δ vs. E_T is linear for