

Electron Photodetachment Spectroscopy of (*E*)- and (*Z*)-Propionaldehyde Enolate Anions. Electron Affinities of the Stereoisomers of Propionaldehyde Enolate Radicals

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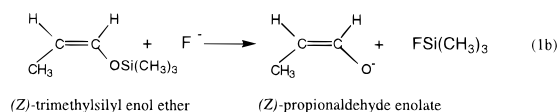
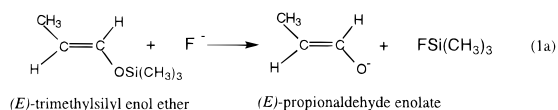
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Stereoisomers can have rather different thermodynamic, kinetic, and spectroscopic properties, so determining the properties of such isomers has been the subject of many studies.¹ Relatively little, however, is known about the properties of stereoisomers of gas-phase ions because it is difficult to independently generate and analyze the ions. Chou and Kass² have reported the synthesis of the (*E*)- and (*Z*)-1-propenyl anions in the gas phase and showed that the two anions have different reactivities. Ho and Squires³ have distinguished the diastereomeric products of gas-phase hydride reductions of alkyl-substituted cyclohexanones by their reactivities. Chyall, Brickhouse, Schnute, and Squires⁴ have addressed the stability of the two stereoisomeric isomers of secondary 2-butanone enolate and calculated their basicities.

We report here the electron photodetachment spectra of the (*E*)- and (*Z*)-isomers of propionaldehyde enolate anion. These ions have different stabilities with respect to their neutral enolate radicals. The anions also show different spectroscopic behavior, consistent with their structures, that allows us to differentiate between them.

Experiments were performed with an ion cyclotron resonance spectrometer (ICR), in which ions were continuously generated and detected, as described previously.⁵ The light source was a Ti:sapphire laser (Lexel 479, bandwidth of $\pm 1 \text{ cm}^{-1}$). We synthesized (*E*)- and (*Z*)-trimethylsilyl enol ethers of propionaldehyde, as outlined by House et al.,^{1d} and confirmed their structures and purities (>98%) by NMR. Fluoride ion (generated from NF_3) was used to displace the trimethylsilyl (TMS) group, producing the corresponding anions (eq 1a,b).



The electron photodetachment spectra are shown in Figure 1. Although the TMS enol ethers are >98% pure, the ions are produced in a reaction whose exothermicity is sufficient to allow isomerization of the enolate if all of the reaction energy is

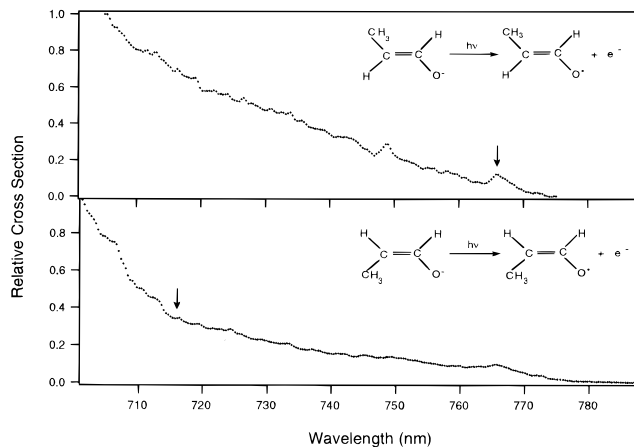


Figure 1. High-resolution photodetachment spectrum of (*E*)-propionaldehyde enolate anion (top panel) and (*Z*)-propionaldehyde enolate anion (bottom panel). Arrows indicate assignment of the electron affinity.

concentrated in the enolate product.⁶ It is possible that each “pure” enolate is contaminated with small amounts of the other isomer (see below). However, the spectra are sufficiently different to assure us that the ions have been characterized.

The (predominantly) (*E*)-isomer shows a fairly sharp onset at 773 nm, with two clearly distinguishable, narrow (4 nm) resonances at 766 and 749 nm.⁷ Above 745 nm, the cross section continues to rise smoothly, with a very slight slope change around 720 nm.⁸ The photodetachment cross section of the (predominantly) (*Z*)-isomer rises above zero at 784 nm. It increases slowly and displays a very small, reproducible resonance at 766 nm, which is broader (10 nm) than the lower energy resonance (766 nm) in the spectrum of the (*E*)-enolate. Because the signal to noise is relatively low, it is difficult to discern any other resonance at higher energies. A dramatic slope change in the cross section is observed at 717 nm; the cross section continues to increase smoothly toward shorter wavelengths. A photodetachment spectrum of the enolate generated by deprotonation of propionaldehyde has been recorded previously over the range 771–743 nm.⁹ The electron affinity determined in that experiment was $37.38 \pm 0.14 \text{ kcal/mol}$. The photodetachment spectrum⁹ resembles the spectrum of the (*E*)-enolate anion; on the basis of the results reported here, the cross section features observed in the previously recorded spectrum can be assigned to the (*E*)-enolate anion. The photoelectron spectrum of the enolate formed by deprotonation of propionaldehyde, possibly a mixture of isomers, shows vibrational structure that was described as complex.¹⁰ The electron affinity

(6) (a) Froehlicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2853. (b) The activation energy necessary to interconvert (*E*)- and (*Z*)-propionaldehyde enolate anions is related to the barrier of rotation around the π -bond, which we calculated to be about 28 kcal/mol. The magnitude of the barrier agrees with the barriers to rotation calculated for similar compounds by Froehlicher et al. (see previous reference). The exothermicity of a reaction of fluoride ion with a trimethylsilyl enol ether derivative is approximately 23 kcal/mol. We estimate that the well depth for the reaction path adds about 10 kcal/mol to the available energy, giving a total of 33 kcal/mol.

(7) (a) The splitting between the two resonances at 766 and 749 nm is 296 cm^{-1} , corresponding to a vibronic transition. Vibrational excitations have been observed for other enolate ions and have been discussed previously. (b) Jackson, R. L.; Hiberty, P. C.; Brauman, J. I. *J. Chem. Phys.* **1981**, *74*, 3705. (c) Marks, J.; Brauman, J. I.; Mead, R. D.; Lykke, K. R.; Lineberger, W. C. *J. Chem. Phys.* **1988**, *88*, 6785.

(8) We find that the photodetachment spectrum of (*E*)-propionaldehyde enolate anion is best described (neglecting the resonances) by two straight lines intersecting at about $715 \pm 4 \text{ nm}$.

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(2) Chou, P. K.; Kass, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 4357.
(3) Ho, Y.; Squires, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 10961.
(4) Chyall, L. J.; Brickhouse, M. D.; Schnute, M. E.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 8681.
(5) (a) The continuous-mode detection provided a large signal-to-noise ratio which allowed detection of small changes (less than 1%) in the ion population. (b) Marks, J.; Drzagic, P. S.; Foster, R. F.; Wetzel, D. M.; Brauman, J. I.; Uppal, J. S.; Staley, R. H. *Rev. Sci. Instrum.* **1987**, *58*, 1460. (c) Wetzel, D. M.; Brauman, J. I. *Chem. Rev.* **1987**, *87*, 607.

determined from the photoelectron spectrum (37.15 ± 0.53 kcal/mol) was in good agreement with the photodetachment threshold measured by ICR, suggesting that it can again be assigned to the (*E*)-enolate radical.

The resonances in the (*E*)-isomer are similar to those observed in other simple enolates; we attribute these resonances to transitions to a dipole-supported state that undergoes autodetachment.^{7b,9,11} The dipole moments of (*E*)- and (*Z*)-propionaldehyde enolate radicals were calculated from *ab initio* molecular orbital calculations, using Gaussian 94, to be 3.34 and 2.93 D, respectively.¹² The spectroscopic results we observe are in good agreement with the model we proposed previously,⁹ in which the lifetime of a dipole-supported state depends on the relative directions of the figure axis and dipole moment of the neutral. The (*E*)-isomer is a near symmetric top, and the dipole moment is aligned close to the figure axis. For such a system, in which it is possible for the molecule to be in a fairly high rotational state but in which the dipole does not rotate, we expect the dipole state to be fairly long lived and thus to show sharp resonances. In contrast, in the (*Z*)-isomer, which is also a near symmetric top, the dipole moment is not aligned with the principal axis. Its dipole-supported state is expected to be shorter lived and thus to show broader resonances. Indeed, these resonances may be too broad for us to observe.⁹

From the photodetachment onset, we can assign the electron affinity for the isomers. For the (*E*)-isomer, we can determine the electron affinity from the observed resonances caused by autodetachment from the dipole-bound state. The photodetachment spectra of acetaldehyde and acetaldehyde-*d*₃ also show a number of resonances.^{7b,11b} For acetaldehyde, the lower energy resonance was assigned to be the 0–0 transition, confirmed by ultra-high-resolution experiments by Lineberger and co-workers.^{11b} They measured an electron binding energy for the dipole-bound state of 6 cm^{-1} relative to the neutral plus electron continuum. Because the structure and dipole moment of the propionaldehyde enolates are roughly similar to those of acetaldehyde enolate, we can infer that the large lower energy resonance (766 nm) in the spectrum of the (*E*)-enolate anion corresponds closely to the electron binding energy of the anion. We assign the electron affinity for the (*E*)-enolate radical to be 37.3 ± 0.2 kcal/mol (1.619 ± 0.007 eV), in good agreement with the value determined from the photodetachment of deprotonated propionaldehyde.^{7b,9,11b,13} There is evidence of a small hot band to the red of the assigned onset.

In the spectrum of the (*Z*)-isomer, we observe a dramatic slope change at 717 nm. We expect the two isomers to display different onsets, as well as different resonances due to dipole-bound states, and assign the 0–0 transition to the onset of that slope change. We believe that the long tail to the red of the slope change is caused by a small amount (~5%) of the (*E*)-isomer present in the sample.¹⁴ In the tail, we can distinguish a small resonance feature, which corresponds to a resonance in the spectrum of the (*E*)-isomer (766 nm). The resonance in the tail is broader than the corresponding resonance in the spectrum of the (*E*)-isomer. For dipole-bound states, excess energy has been shown to cause shorter lifetimes and thus broader resonances.¹⁵ We presume that some of the isomerized (*E*)-enolate has excess vibrational energy and has not thermalized completely.¹⁶ Given that a larger fraction (than usually expected for ions trapped in the ICR for extended periods of time) of the isomerized (*E*)-enolate is excited, the tail at wavelengths below 773 nm in the spectrum of the predominantly (*Z*)-isomer can be assigned to a hot band of the isomerized (*E*)-enolate.

On this basis, we determine the onset for adiabatic electron detachment at 715 ± 5 nm,¹⁷ yielding an electron affinity for the (*Z*)-radical of 40.0 ± 0.3 kcal/mol (1.73 ± 0.01 eV).¹⁸ The (*E*)-isomer appears to also contain small amounts (~7%) of the corresponding (*Z*)-isomer, indicated by the slight slope change at about 720 ± 5 nm in the spectrum of the (*E*)-enolate.⁸ A slope change at about 725 ± 20 nm was also observed in the low-resolution spectrum of the enolate anions formed by the deprotonation of propionaldehyde, indicating that the anions were again a mixture of (*E*)- and (*Z*)-isomers.¹⁹

In summary, we have generated the (*E*)- and (*Z*)-enolates of propionaldehyde and have found them to possess different intrinsic properties. The anion stabilities relative to the neutral radicals differ noticeably, as does their spectroscopic behavior. The electron affinity of (*E*)-propionaldehyde enolate radical was measured to be 37.3 ± 0.2 kcal/mol and that of the corresponding (*Z*)-radical to be 40.0 ± 0.3 kcal/mol. Finally, the spectrum of the (*E*)-isomer displayed resonances attributed to dipole-bound states, while the spectrum of the (*Z*)-isomer does not, consistent with our model for long-lived dipole states.

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(13) The electron binding energy in these enolate anions is very small, as shown for acetaldehyde enolate. The error associated with the assignment of the electron affinity to the center of the vibrational band cannot exceed the width of the resonance toward higher and lower wavelengths.

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(14) (a) Generally, we do not expect to see hot bands because molecules are trapped in the ICR cell for 100–1000 ms and can relax by radiative and collisional processes. Even though the desilylation reaction is reasonably exothermic, anions formed in this reaction usually appear to thermalize before photodetachment, and the fraction of excited anions should be fairly small relative to the fraction of relaxed anions (see next reference). (b) Brinkman, E. A.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1994**, *116*, 8304.

(15) Marks, J. Ph.D. Dissertation, Stanford University, 1986.

(16) It is not clear why this enolate did not fully relax.

(17) We determine the onset of the slope change by taking linear least-squares fits to the higher and lower energy sections of the photodetachment curve. The intercept of the two best fit curves then corresponds to the detachment threshold. We have chosen an error limit of ± 5 nm to easily accommodate any possible variations in the intercept of the two lines due to different fitting parameters.

(18) Our calculational results (Gaussian 94, geometry optimizations using HF/6-31+G* level followed by MP2 single-point calculations) also predict the electron affinity of the (*Z*)-radical to be greater than that of the (*E*)-radical by about 2 kcal/mol. We found the anion of the (*Z*)-isomer to be more stable than that of the (*E*)-isomer by 2 kcal/mol and found both radicals to have similar stabilities.

(19) In the CW ICR experiment, propionaldehyde enolate anions were formed by the exothermic deprotonation of propionaldehyde with fluoride ion and may not have reached equilibrium concentration before photodetachment.