Electron Photodetachment Spectroscopy of Polyene Anions. Electron Affinities of Pentadienyl and Heptatrienyl Radicals

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Abstract: The relative cross sections for photodetachment of electrons from pentadienyl and heptatrienyl anions have been measured in the visible and near UV. An ion cyclotron resonance spectrometer was used to generate, trap, and detect the negative ions; an arc lamp with a grating monochromator was the light source. Resonances at 363 ± 10 and 430 ± 5 nm are associated with autodetaching $\pi \rightarrow \pi^*$ states of $C_5H_7^-$ and $C_7H_9^-$, respectively. The electron affinities of the pentadienyl and heptatrienyl radicals have been determined as 0.91 ± 0.03 and 1.27 ± 0.03 eV, respectively.

In recent years the electronic spectroscopy of negative ions has been the subject of increasing interest in terms of both basic theory as well as practical application. Negative ions in general are not amenable to standard optical absorption measurements of electronic spectra unless they are present in solution[1] or trapped in low temperature matrices.[2] These media, which permit high concentrations, provide stabilizing interactions which can cause shifts in the electronic absorption features of the solvated ion relative to the free ion. Aspects of the spectroscopy of molecular negative ions in the gas phase have been studied extensively in recent years by low energy electron scattering[3] and electron impact[4] methods. These methods, however, are generally applicable only to ions formed by adding an electron to a stable neutral molecule and are less useful for studying the spectroscopy of closed-shell anions, many of which are of importance in ion–molecule reactions. In this work we investigate electron photodetachment as a method for probing the electronic spectra of such stable gas phase negative ions.

Stable negative ions usually have quite low electron binding energies, typically in the range 0–4 eV. Thus most low-lying electronic states of negative ions will occur at energies greater than that required to remove an electron. A negative ion which undergoes a transition to an excited state will therefore often have sufficient energy for electron loss (autodetachment) to occur. The autodetaching excited state will have a finite lifetime, which is governed by the nature of the coupling of the excited state with the continuum. In the photodetachment cross section an autodetaching state will appear as a resonance whose intensity is determined by the oscillator strength for the optical transition to the excited state and whose width is determined by the autodetachment lifetime of the excited state.[5]

The photodetachment cross section of a polyatomic negative ion should show a manifold of autodetaching resonances corresponding to vibronic transitions to the excited negative ion state. Autodetachment resonances in general may be quite asymmetric.[5] However, when the optical transition has a large oscillator strength, the resonances may appear similar to optical absorption peaks superimposed on the continuum cross section. In this case the resonant state wave function is dominated by closed-channel components often encountered in electron scattering and electron impact experiments.[3,4,6] Peaks presumably of this type have been observed in the photodetachment cross sections of phenoxide and thiophenoxide anions;[7] autodetaching negative ion states were proposed as a possible explanation. Maxima in the photodetachment cross sections of enolate anions have also recently been suggested as being due to electronic transitions to autodetaching negative ion states.[8] However the electronic transitions which cause this behavior have yet to be experimentally characterized and assigned in a systematic manner.

In this paper we report electron photodetachment cross sections for the pentadienyl and heptatrienyl anions. In these polyene anions the lowest optically allowed[9,10] transition is expected to be the intense $^1A_2 \rightarrow {}^1B_2$ transition. This transition may be easily characterized both by the red shift which occurs with increasing conjugation length and by its high intensity. Peaks are observed in the cross sections for the pentadienyl and heptatrienyl anions and are assigned to this transition. Semiempirical PPP calculations indicate that these peaks occur at resonable wavelengths for the lowest $\pi \rightarrow \pi^*$ transition in the anions. The electron affinities of the pentadienyl and heptatrienyl radicals are estimated from the photodetachment thresholds.

Experimental Section

All photodetachment measurements were carried out as previously described[11] using a Varian V-5900 ion cyclotron resonance spectrometer with a modified square cell design. Ion residence times of 0.5–1.0 s could be obtained by using high trapping potentials (2.0–3.0 eV), moderate source drift potentials (0.2–1.0 eV), low analyzer drift potentials (<0.4 eV), and pressures of about 10^{-6} Torr. The light source which was employed consisted of a 1000-W xenon arc lamp used with a grating monochromator as previously described.[11]

Pentadienyl and heptatrienyl anions were formed from *trans*-1,3-pentadiene and 1,3,6-heptatriene, respectively, by using F^- to abstract a proton from these compounds. The F^- was formed from NF_3 by dissociative electron attachment at 1.7 eV (electron energy minus trapping voltage). The neutral pentadiene and heptatriene were obtained from Aldrich Chemical Co., and were used without additional purification.

Results

Figure 1 presents the experimental photodetachment cross sections for the pentadienyl and heptatrienyl anions, respectively. These cross sections show intense peaks at 363 ± 10 and 430 ± 5 nm, respectively. The photodetachment cross section for allyl anion (included for comparison in Figure 1), which has been previously reported and discussed in detail,[12] shows a rise below 400 nm suggesting a similar peak occurring below 300 nm.

The photodetachment thresholds for the pentadienyl and heptatrienyl anions are 1400 ± 39.6 and 1000 ± 23.8 nm, respectively. The error limits reflect the experimental bandwidth in the threshold regions. Based on our previous results, we have no reason to believe that these ions are strongly excited vibrationally, and we also expect the 0–0 transition to have reasonable intensity, although at present we cannot prove the validity of these assumptions. However, the error limits are fairly conservative, and if we assume that the contribution of hot band transitions to each of the cross sections in Figure 1 is small, the electron affinities of the pentadienyl and heptatrienyl radicals may be determined by subtracting the exper-
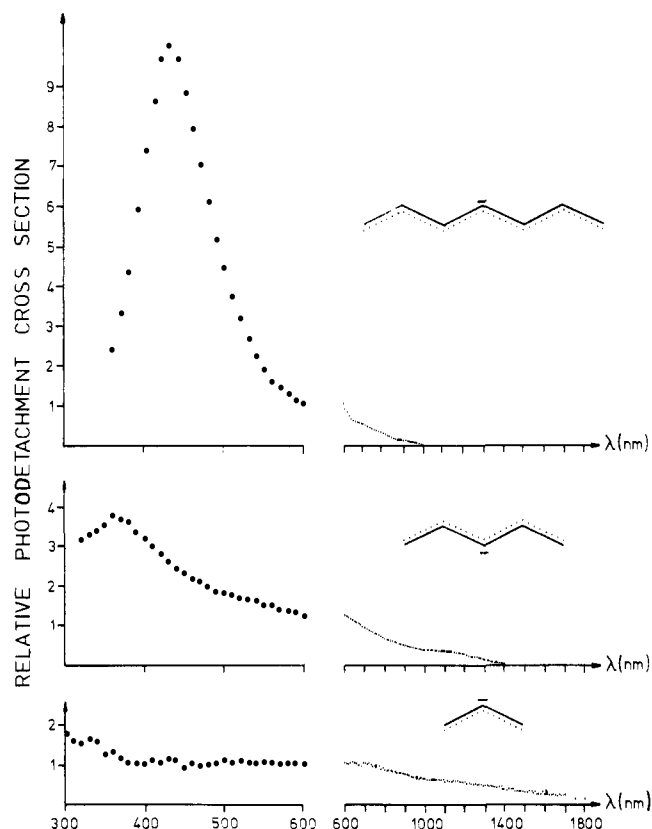
Figure 1. Relative photodetachment cross sections for heptatrienyl, pentadienyl, and allyl anions, normalized to the same value at 0.5 eV above threshold. Fractional signal decreases varied from about 10% at maximum to 0.1–0.25% near threshhold.

imental bandwidth from each observed threshold. This gives electron affinities of 0.91 ± 0.03 (21.0 ± 0.7 kcal/mol) and 1.27 ± 0.03 eV (29.3 ± 0.7 kcal/mol) for the pentadienyl and heptatrienyl radicals, respectively. For comparison the electron affinity of the allyl radical has been previously determined[12] to be 0.55 ± 0.054 eV (12.7 ± 1.2 kcal/mol).

Discussion

The peaks reported here in the photodetachment cross sections of polyene anions closely resemble the $\pi \rightarrow \pi^*$ absorption peaks typically seen in the electronic spectra of neutral conjugated molecules. The cross section for autodetachment of $\pi \rightarrow \pi^*$ excited states in anions will resemble the optical absorption spectra for transitions to bound states, if the lifetime is relatively long on the atomic scale.[3a] Evidence that the peaks observed in Figure 1 are due to $\pi \rightarrow \pi^*$ transitions is provided by the pronounced red shift in peak position as the length of the conjugated system is increased, behavior which is characteristic of such transitions. In addition these peaks are extremely intense relative to the continuum, a result which is expected for the lowest $^1A_2 \rightarrow {}^1B_2$ transition in the polyene anions.[10] Thus these peaks may be identified as corresponding largely to the lowest optically allowed transition in the anion, $^1A_2 \rightarrow {}^1B_2$, followed by autodetachment of the resultant excited state.

The positions of the $\pi \rightarrow \pi^*$ transitions in polyene anions occur at significantly lower energies than do the corresponding transitions in the neutral molecules of similar conjugation length.[13] A major source of this difference is the increased shielding of the core. In neutrals each electron senses the potential of N positive charges of the core and $N - 1$ negative charges of the other electrons, while in anions the number of positive charges of the core is balanced by an equal number of screening electrons. The electrons are thus much more weakly

bound in anions. This effect causes a more diffuse spatial distribution of the electrons,[14] and results, in essence, in an increased conjugation length.

The $\pi \rightarrow \pi^*$ transition energies of polyene anions may be analyzed in terms of the free electron molecular orbital (FEMO) model of Kuhn.[15] In this model the π electrons are confined to an infinite square well potential having a width determined by the length of the conjugated system. By allowing the width of this square well to extend beyond the ends of the conjugated system we may approximate the added diffuseness of negative ion orbitals. Following the treatment of Kuhn,[15] this model gives the positions of the $\pi \rightarrow \pi^*$ transitions as 236, 363, and 490 nm for the allyl, pentadienyl and heptatrienyl anions respectively. The distance which the well extends beyond the ends of the conjugated system was adjusted to give agreement for pentadienyl anion and was 1.59 Å. Based on these results the FEMO model does not give particularly good agreement with experiment for the positions of $\pi \rightarrow \pi^*$ transitions for these anions.

Hückel (HMO) theory predicts the transition energies of polyene anions to lie between those for the two neutral polyenes with one carbon more and one carbon less, in poor agreement with the experiment.[13] Clearly, a many electron treatment such as PPP should be better. PPP calculations[16] using parameters[17] optimized for neutral aromatic hydrocarbons predict a red shift of the lowest allowed $\pi \rightarrow \pi^*$ transition ($A_2 \rightarrow B_2$) for the allyl, pentadienyl, and heptatrienyl anions compared with the neutral polyenes. This effect, however, is still less pronounced than that found experimentally. In terms of the parameters used in the PPP treatment the increased diffuseness of the basis orbitals implies that their energy (α) and the resonance integral (β), both of which are related to the interaction of the valence electrons and the core, will be lowered in magnitude. For a hydrocarbon, changes in α will not affect the predicted transition energies within the assumptions of the treatment, since the ground and excited states are shifted by the same amount. A lower absolute value of β, however, will decrease the splitting of the orbitals and thus[18] the transition will be red shifted. The third parameter, the electron repulsion integral (γ), should be lower in the anions than in neutral molecules due to the increased diffuseness of the basis orbitals. Lowering γ will also result in a red shift of the $A_2 \rightarrow B_2$ transitions: The electron repulsion contribution to the orbital energy is larger for the LUMO than the HOMO, in which nodes alternate with nonzero coefficients, and therefore diminishing the electron-electron repulsion lowers B_2 more than A_2. However, although the qualitative changes resulting from reparametrization are predictable, it will be necessary to obtain more experimental information in order to make a quantitative effort worthwhile.

The electron affinities (EA's) of the corresponding radicals are difficult to calculate because of the reorganization of the electronic structure of the molecules on electron detachment. Indeed, in the HMO approximation all the EA's are identical. Interestingly, however, the EA's correlate with the delocalization energies for these three systems[19,20] and the correlation extrapolates to zero EA for a nondelocalized radical. Other estimates[20,21] of the EA for nondelocalized radicals are close to zero.

For closed shell anions, the electron detachment process is analogous to the ionization of a closed shell neutral, and we can apply Koopmans' theorem.[22] Indeed a linear correlation of the EA's of the allyl, pentadienyl, and heptatrienyl radicals with the highest occupied molecular orbitals in our PPP calculations is found, although the absolute magnitudes of the energies do not agree. Applying empirical corrections for the polarization of the σ core and the valence basis orbitals and reoptimizing the orbitals of the radicals, Hoyland and Goodman have calculated the electron affinities of the allyl and pentadienyl

radicals to be 0.53 and 0.97 eV, respectively.[23] The excellent agreement of these values with the experimental electron affinities indicates the potential of the method used by these workers for determining the electron affinities of π radicals.

Conclusions

Photodetachment cross section experiments have been shown to be a sensitive method for measuring the electronic spectra of gas phase negative ions. The positions of $\pi \rightarrow \pi^*$ transitions in some polyene anions are found systematically to occur at longer wavelengths than those for neutral molecules of comparable conjugation. This observation provides evidence that π orbitals in delocalized negative ions are significantly more diffuse than those in neutrals. Finally the experimental electron affinities of polyene radicals are shown to be linearly correlated with both the HMO delocalization energies in the anions and the HOMO energies from PPP calculations on the anions. These correlations may provide a useful method for estimating the electron affinities of other polyene radicals.

References and Notes

(1) For example, see B. Bockrath and L. M. Dorfman, *J. Am. Chem. Soc.*, **96**, 5708 (1974); A. Streitwieser, Jr., and J. I. Brauman, *ibid.*, **85**, 2633 (1963).
(2) See E. T. Kaiser and L. Kevan, Ed., "Radical Ions", Wiley-Interscience, New York, 1968.
(3) (a) D. Spence, *J. Chem. Phys.*, **66**, 669 (1977); (b) P. D. Burrow and K. D. Jordan, *Chem. Phys. Lett.*, **36**, 594 (1975); (c) K. D. Jordan, J. A. Michejda, and P. D. Burrow, *ibid.*, **42**, 227 (1976).
(4) (a) R. N. Compton, L. G. Christophorou, G. S. Hurst, and P. W. Reinhardt, *J. Chem. Phys.*, **45**, 4634 (1966); (b) R. N. Compton, L. G. Christophorou, and R. H. Huebner, *Phys. Lett.*, **23**, 656 (1966); (c) W. T. Naff, R. N. Compton, and C. D. Cooper, *J. Chem. Phys.*, **57**, 1305 (1972); (d) C. D. Cooper and R. N. Compton, *ibid.*, **59**, 3550 (1973); (e) *ibid.*, **60**, 2424 (1974); (f) J. A. Stockdale, F. T. Davis, R. N. Compton, and C. E. Klots, *ibid.*, **60**, 4279 (1974); (g) C. D. Cooper, W. T. Naff, and R. N. Compton, *ibid.*, **63**, 2752 (1975).
(5) U. Fano, *Phys. Rev.*, **124**, 1866 (1961).
(6) G. J. Shulz, *Phys. Rev.*, **125**, 229 (1962); A. Herzenberg and F. Mandl, *Proc. R. Soc. London, Ser. A*, **270**, 48 (1962).
(7) J. H. Richardson, L. M. Stephenson, and J. I. Brauman, *J. Chem. Phys.*, **62**, 1581 (1975); *J. Am. Chem. Soc.*, **97**, 2967 (1975).
(8) A. H. Zimmerman, K. J. Reed, and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 7203 (1977); A. H. Zimmerman and J. I. Brauman, *J. Chem. Phys.*, **66**, 5823 (1977).
(9) This is probably not the lowest electronic transition in neutral polyenes. See B. S. Hudson and B. Kohler, *Annu. Rev. Phys. Chem.*, **25**, 437 (1974). However it is certainly the lowest transition which has sufficient optical intensity to be easily observed in the spectrum. Because correlation effects are likely to be less important in the relatively diffuse anion, this may also be the lowest energy transition as well.
(10) C_{2v} symmetry is assumed for the polyene anions.
(11) K. C. Smyth and J. I. Brauman, *J. Chem. Phys.*, **56**, 1132 (1972).
(12) A. H. Zimmerman and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 3565 (1977).
(13) For example the lowest optically allowed $\pi \rightarrow \pi^*$ transitions in ethylene, butadiene, hexatriene, and octatetraene occur at 162.5, 217.0, 251, and 304 nm, respectively; see A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1961, p 208.
(14) For examples, see C. J. Roothaan and A. W. Weiss, *Rev. Mod. Phys.*, **32**, 194 (1960); E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, *Phys. Rev.*, **133**, 1274 (1964); P. E. Cade, *J. Chem. Phys.*, **47**, 2390 (1967); K. M. Griffing and J. Simons, *ibid.*, **62**, 535 (1975); E. Andersen and J. Simons, *ibid.*, **65**, 5393 (1976).
(15) H. Kuhn, *J. Chem. Phys.*, **17**, 1198 (1949).
(16) (a) R. D. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953). (b) The off-diagonal electron–electron repulsion integrals were calculated according to N. Mataga and K. Nishimoto, *Z. Phys. Chem. (Frankfurt am Main)*, **13**, 140 (1957).
(17) P. Hochmann, R. Zahradnik, and V. Kvasnicka, *Collect. Czech. Chem. Commun.*, **33**, 3478 (1968).
(18) Configuration mixing of all singly excited configurations does not affect the predicted transitions significantly.
(19) (a) The delocalization energies for allyl and pentadienyl anions are from C. A. Coulson and A. Streitwiesser, Jr., "Dictionary of Pi Electron Calculations", Pergamon Press. New York, N.Y., 1965. (b) The delocalization energy for heptatrienyl anion is from A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations", Vol. 1, Pergamon Press, New York, N.Y., 1965, p 12.
(20) D. S. Marynick and D. A. Dixon, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 410 (1977).
(21) J. E. William, Jr., and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **97**, 2634 (1975).
(22) T. Koopmans, *Physica*, **1**, 104 (1934).
(23) J. R. Hoyland and L. Goodman, *J. Chem. Phys.*, **36**, 21 (1962).

Photoelectron Spectroscopy of Carbonyls. Lone-Pair Interactions in α-, β-, γ-, and δ-Dicarbonyls

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Abstract: The ionization of the nonbonding electrons, n_+ and n_-, of 73 dicarbonyls (38 α-, 24 β-, 8 γ-, and 3 δ-) have been surveyed experimentally (ultraviolet photoelectron spectroscopy) and computationally (CNDO/s and CNDO/2). Apart from certain readily rationalized exceptions, it is shown that the energy split of the n_+/n_- ionization events is primarily determined by the separation of the two carbonyl groups; that the splitting mechanism involves through-bond interaction with skeletal σ orbitals; and that the Franck–Condon band shapes of $I(n_+)$ and $I(n_-)$ are determined by the nature of the intermixed skeletal σ orbitals. A simple algorithm for $I(n_+)/I(n_-)$ splittings and band shapes is presented.

Introduction

Much work has been invested[1-21] in the ultraviolet photoelectron spectroscopy (UPS) of carbonyl compounds in order to identify the mechanism by which carbonyl groups interact among themselves and with other functional groups. However, many of the UPS assignments are unsatisfactory since they are largely based on the isomorphism between quantum chemical and UPS data sets implied by Koopman's theorem.[22]

A "simple dicarbonyl compound" is one which contains neither heteroatoms (other than two oxygens) nor carbon-carbon unsaturation. The two highest occupied MOs of simple dicarbonyls consist[1,2,12] predominantly of linear combinations