5074 *J. Am. Chem. Soc.* **1996,** *118,* 5074−5082

Ultraviolet Photoelectron Spectroscopy of Some $C_7H_7^-$ Isomers: Quadricyclanide, Norbornadienide, Cycloheptatrienide, and 1,6-Heptadiynide

Robert F. Gunion,[†] William Karney,[‡] Paul G. Wenthold,[†]
Weston Thatcher Borden,*,[‡] and W. C. Lineberger*,[†]

Contribution from the JILA and Department of Chemistry and Biochemistry,
University of Colorado, Boulder, Colorado 80309-0440, and Department of Chemistry,
University of Washington, Seattle, Washington 98195

Received November 30, 1995[⊗]

Abstract: The 351 nm photoelectron spectra of several isomers of $C_7H_7^-$, obtained by deprotonating quadricyclane, norbornadiene, 1,6-heptadiyne, and cycloheptatriene, are reported. Quadricyclane can be deprotonated from either of two distinct sites by amide anion. The electron affinities (EAs) of the two corresponding $C_7H_7^\bullet$ isomers are 0.868(6) and 0.962(6) eV, with one well-resolved vibration observed for each state, at 909(20) and 826(20) cm^{-1}, respectively. Deprotonation of norbornadiene by amide anion leads to formation of one ionic isomer with a binding energy of 1.286(6) eV. Detachment to form an excited state of the neutral is also observed, with a vertical detachment energy (VDE) of 2.8(1) eV. Three vibrational modes are resolved in the ground state region of the spectrum, and one excited state vibration is observed. 1,6-Heptadiyne is deprotonated by hydroxide at two sites, the end carbon (C_1) and the third carbon (C_3), to produce isomers with binding energies of 3.037(10) and 1.132(6) eV, respectively. One vibration at 500(20) cm^{-1} is strongly active in the C_3-deprotonated portion of the spectrum. Reaction of cycloheptatriene with hydroxide or amide produces a mixture of products at 91 amu which includes the isomer of $C_7H_7^-$ corresponding to abstraction from the methylene group. The corresponding neutral has an EA $\leq$ 0.43 eV, in agreement with earlier estimates obtained from thermochemical cycles. The remaining products are assigned to vinyl systems with transitions in the photoelectron spectrum to the ground and first excited states. The measured VDEs of these states are 1.48(1) and 2.97(1) eV, respectively. The spectrum of benzyl anion appears in the spectra of all of the other $C_7H_7^-$ isomers, probably as a result of toluene contamination in the precursors.

Introduction

The interpretation of photoelectron spectra of large organic molecular anions (>4 heavy atoms) has rarely been attempted because of the potential for complexity due to large numbers of vibrational modes, electronic states, and unidentifiable isomers. However, we have found that the photoelectron spectra of some large systems with rigid frames can prove to be simple,[1] enabling the extraction of molecular properties not easily probed with other methods. Possibly the most valuable information derived in this way is the thermodynamic information that can be derived from the measured electron affinities and excited state term energies. In an effort to clarify the effects of structure on negative ion photoelectron spectra, we have taken advantage of the fact that many C_7H_8 isomers are commercially available to obtain photoelectron spectra of several isomers of $C_7H_7^-$. The identifiable $C_7H_7^-$ isomers for which spectra have been obtained are depicted in Figure 1.

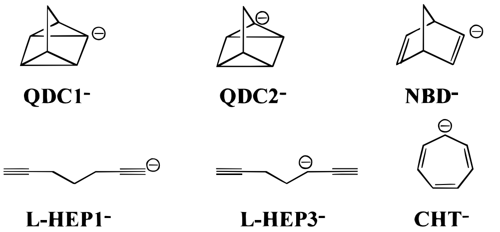

Figure 1. Structures of the $C_7H_7^-$ isomers identified as the signal carriers for the photoelectron spectra presented in Figures 3−6. QDC1$^-$, 1-quadricyclanide; QDC2$^-$, 2-quadricyclanide; NBD$^-$, norbornadienide; L-HEP1$^-$, 1-(1,6-heptadiynide); L-HEP3$^-$, 3-(1,6-heptadiynide); CHT$^-$, cycloheptatrienide.

The accompanying investigation[2] into the reactivity of quadricyclanide anion is the most recent example of the complementary information made available by negative ion photoelectron spectroscopy and flowing afterglow/selected ion flow tube (FA/SIFT) experiments. Similar collaborations between these laboratories include measurements of the electron affinities and gas-phase acidities of C_3 hydrocarbons[3] (allene, methyl acetylene, and propargyl radical) and of ethylene and acetylene,[4] through which the CH bond dissociation energies were obtained. In cases where the FA/SIFT technique has been used to measure gas-phase acidities in the past, the bond energies can be determined using the EA's measured in this study. This is the case for cycloheptatriene and toluene[5] and for norbornadiene.[6] The FA/SIFT technique is also used to determine the structures of the $C_7H_7^-$ anions resulting from deprotonation of

---

[†] JILA and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0440.

[‡] Department of Chemistry, University of Washington, Seattle, WA 98195.

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

(1) Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spec. Ion Proc.* **1992**, *117*, 601.

(2) Lee, H.-S.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1996**, *118*, 5068.

(3) Robinson, M. S.; Polak, M. L.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C. *J. Am. Chem. Soc.* **1995**, *117*, 6766.

(4) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750.

(5) DePuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, *14*, 146. A slightly revised but much more precise value for ΔH_{acid}(toluene) of 382.3 ± 0.4 kcal/mol has been obtained: Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B. *Int. J. Mass Spectrom. Ion Processes*, in press.

S0002-7863(95)04026-1 CCC: $12.00

the C_7H_8 precursors. In this way the products of the reactions of quadricyclane,[2] cycloheptatriene,[5] toluene,[5] and norbornadiene[6] with ionic bases were found to possess the structures shown in Figure 1. Since the thermochemistry of the deprotonated quadricyclane ion is fully described in the accompanying paper (*J. Am. Chem. Soc.* **1996**, *118*, 5068), it is not emphasized in this paper.

Several additional studies have been performed on gas-phase $C_7H_7^-$ anions. In an ion cyclotron resonance (ICR) experiment,[7] the CHT^- (tropyl anion, Figure 1) and benzyl (BEN^-) anions were formed by the reaction of cycloheptatriene and toluene, respectively, with CH_3O^-, and the resulting multiphoton electron detachment spectra were shown to be different, confirming that the products are distinct isomers of $C_7H_7^-$. The photodetchment spectrum of a third isomer of $C_7H_7^-$, assumed to be norbornadienide (NBD^-, Figure 1) formed from the reaction of norbornadiene with NH_2^-, was also reported. In a study using Fourier transform mass spectrometry,[8] the reaction of cycloheptatriene with ND_2^- and OD^- formed BEN^- while reaction with CD_3O^- resulted formation of CHT^-, providing evidence that the barrier to isomerization is overcome by reaction with the stronger bases but not with CD_3O^-. The observation of isomerization in this case and not in the previous study that used OH^- to generate the ion[5] was explained in light of the higher pressure of the FA source (*ca.* 1 Torr vs 10^{-6} Torr), where collisional cooling may occur more quickly than the isomerization. In other studies, the gas-phase acidity of cycloheptatriene was measured using forward and reverse proton transfer rate measurements in an ICR,[9] and the methylenic C−H bond energy has been determined.[10] The geometry and heat of formation of a slightly different $C_7H_7^-$ isomer, 7-norbornadienyl, is included in MINDO/2 calculations[11] of the 7-norbornyl, 7-norbornenyl, and 7-norbornadienyl anions, radicals, and cations.

This paper is organized as follows: since the $C_7H_7^\bullet$ and C_7H_8 isomers are as important to the present investigation as the isomers of $C_7H_7^-$, previous literature concerning them is summarized first. Next, the experiment is described briefly with an emphasis on the methods and conditions for ion production. The results and discussion follow, with the presentation and interpretation of each of the photoelectron spectra of the $C_7H_7^-$ isomers in turn.

Relevant $C_7H_7^\bullet$ and C_7H_8 Studies

Relevant $C_7H_7^\bullet$ Studies. Previous investigations into the C_7H_7 radical surface include a finding[12] that 1-quadricyclyl ($QDC1^\bullet$) rearranges in solution to bicyclo[3.2.0]hepta-3,6-dien-2-yl radical ($BHD^\bullet$) and not to 7-norbornadienyl, unlike the case for the cation. The same authors used ESR to deduce[13] that C_7 in 7-norbornadienyl radical is more pyramidal than the dehydrogenated carbon in cyclopropyl radical. The ESR spectra of radicals produced by X-ray irradiation of quadricyclane in an adamantane matrix appear[14,15] to correspond to the $BHD^\bullet$ radical, which subsequently rearranges to $CHT^\bullet$ radical. The same studies[14,15] report that 7-norbornadienyl does not rearrange to $BHD^\bullet$ under similar conditions. In connection with this study, preliminary ab initio calculations have been performed[2,16] to determine the electron affinities of the $QDC^\bullet$ radicals corresponding to the QDC^- anions in Figure 1. These calculations predict a lower electron affinity for $QDC1^\bullet$ than for $QDC2^\bullet$.

Relevant C_7H_8 Studies. The literature describing C_7H_8 isomers is extensive. Investigations into the properties of quadricyclane and norbornadiene are almost invariably linked, in large part because the photoisomerization of norbornadiene to quadricyclane, first observed[17,18] in 1961, was recognized as a possible route to storing energy in solar cells.[19,20] The through-bond and through-space interactions of the π bonds in norbornadiene also make an interesting avenue of chemical exploration,[21] and, in a sense, quadricyclane represents the extreme of through-space interaction. This interaction has been explored most fully in the photoelectron spectrum of neutral norbornadiene[22,23] and of quadricyclane, norbornane, and norbornene.[24−26] These studies find that through-space interaction is most important in norbornadiene, as concluded from the higher energy of the antisymmetric combination of the π orbitals relative to the symmetric combination,[26] and confirmed in later calculations.[22,23] Recently, the catalyzed conversion of quadricyclane to norbornadiene in CCl_4 was monitored by Raman spectroscopy.[27] Several excited state properties of norbornadiene have also been calculated.[28] An attempt to determine the structure of quadricyclane was made using gas-phase electron diffraction spectroscopy,[29] and the same data were reinvestigated several years later[30] when the results of the first study did not agree with a subsequent ab initio calculation.[24] Norbornadiene was studied using microwave Fourier transform spectroscopy,[31] and a similar investigation of quadricyclane followed.[32] The infrared and Raman spectra of solid norbornadiene[33] and quadricyclane[34] were obtained at various temperatures and pressures.

Literature concerning 1,6-heptadiyne includes two photoelectron spectroscopic studies,[35,36] one of which[35] also presents ab initio calculations to help compare the through-space and

---

[6] Lee, R. E.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 5078.

[7] Wight, C. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6499.

[8] White, R. L.; Wilkins, C. L.; Heitkamp, J. J.; Staley, S. W. *J. Am. Chem. Soc.* **1983**, *105*, 4868.

[9] Bartmess, J. E.; Scott, J. A.; McIver, R. T.*J. Am. Chem. Soc.* **1979**, *101*, 6046. The gas-phase acidity quoted in the text is an updated value from the NIST Negative Ion Energetics Database, Version 3.00, NIST Standard Reference Database 19B, October 1993.

[10] Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.

[11] Dewar, M. J. S.; Schoeller, W. W. *Tetrahedron* **1971**, *27*, 4401.

[12] Sugiyama, Y.; Kawamura, T.; Yonezawa, T. *J. Am. Chem. Soc.* **1978**, *100*, 6525.

[13] Sugiyama, Y.; Kawamura, T.; Yonezawa, T. *J. Chem. Soc., Chem. Commun.* **1978**, *1978*, 804.

[14] Brandes, D.; Lange, F.; Sustmann, R. *Tetrahedron Lett.* **1980**, *21*, 265.

[15] Sustmann, R.; Brandes, D.; Lange, F.; Nuchter, U. *Chem. Ber.* **1985**, *118*, 3500.

[16] Karney, W., private communication.

[17] Dauben, W. G.; Cargill, R. L. *Tetrahedron* **1961**, *15*, 197.

[18] Hammond, G. S.; Turro, N. J.; Fischer, A. *J. Am. Chem. Soc.* **1961**, *83*, 4674.

[19] Canas, L. R.; Greenberg, D. B. *Solar Energy* **1985**, *34*, 93.

[20] Archer, M. D.; Bolton, J. R. *J. Phys. Chem.* **1990**, *94*, 8028.

[21] Hoffman, R. *Acc. Chem. Res.* **1971**, *4*, 1.

[22] Galasso, V. *Chem. Phys.* **1989**, *138*, 231.

[23] Von Niessen, W.; Diercksen, G. H. F. *J. Electron Spec.* **1979**, *16*, 351.

[24] Van Alsenoy, C.; Scarsdale, J. N.; Schäfer, L. *J. Comput. Chem.* **1982**, *3*, 53.

[25] Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213.

[26] Heilbronner, E.; Martin, H.-D. *Helv. Chim. Acta* **1972**, *55*, 1490.

[27] Ford, J. F.; Mann, C. K.; Vickers, T. J. *App. Spectrosc.* **1994**, *48*, 592.

[28] Galasso, V. *Chem. Phys.* **1991**, *153*, 13.

[29] Mizuno, K.; Fukuyama, T.; Kuchitsu, K. *Chem. Lett.* **1972**, *1972*, 249.

[30] Doms, L.; Geise, H. J.; Alsenoy, C. V.; Enden, L. V. D.; Schafer, L. *J. Mol. Struct.* **1985**, *129*, 299.

[31] Vogelsanger, B.; Bauder, A. *J. Mol. Spec.* **1988**, *130*, 249.

[32] Vogelsanger, B.; Bauder, A. *J. Mol. Spec.* **1989**, *136*, 62.

[33] Kawai, N. T.; Gilson, D. F. R.; Butler, I. S. *J. Phys. Chem.* **1990**, *94*, 5729.

[34] Kawai, N. T.; Gilson, D. F. R.; Butler, I. S. *J. Phys. Chem.* **1992**, *96*, 8556.

through-bond interactions between the two acetylene groups. Further studies are difficult to locate, and a comparison of the deprotonated 1,6-heptadiyne photoelectron spectrum with the corresponding photoelectron spectra of acetylide[37] (C_2H^-) and allenyl[3] (H_2CCCH^-) anions is the most useful tool for interpreting the results presented here.

Investigations into the properties of cycloheptatriene have included vibrational spectroscopy of the solid,[38] electron spin resonance matrix study of the radical cation,[39] resonance Raman study in solution of the (1,7)-hydrogen shift in cycloheptatriene,[40,41] and several investigations[42-55] into the isomerization of cycloheptatriene to toluene. These studies start with the original observation[42] in 1962 that photoisomerization of cycloheptatriene at low pressures produces toluene, most likely by formation of an excited singlet state which converts to an excited vibration of the ground electronic state before collisional isomerization to toluene. The Troe group has investigated in detail the photoisomerization of cycloheptatriene to toluene[43-46] and the subsequent hydrogen atom loss to form BEN^- radical.[47,48] A numerical solution to the master equation for non-steady-state reactions was presented[49] and compared with the findings of the Troe group. The dissociation rate of toluene to form BEN^- was measured by Ikeda et al.,[50] and the cycloheptatriene-toluene isomerization rate was measured using coherent anti-Stokes Raman spectroscopy.[51] The rate of formation of hydrogen atoms to form BEN^- from the cycloheptatriene-toluene isomerization process was measured,[52] and the rate of the excited state to ground state conversion in cycloheptatriene was measured.[53] On the cationic C_7H_8 surface, the isomerization can proceed in the opposite direction, as the toluene cation isomerizes to the cycloheptatriene cation,[54] though this can be a difficult reaction to study.[55]

Experimental Section

The negative ion photoelectron spectrometer has been described in detail previously[56,57] and more concisely in a recent review[58] and so will be described only briefly. All ions studied in this paper were formed in a flowing afterglow ion source by the reaction of the precursors (C_7H_8) with hydroxide or amide anions. The source conditions will be described in more detail below.

Once formed, the ions are extracted into a low pressure region, accelerated to 735 eV, mass-selected in a Wien filter, and decelerated to 40 eV prior to passing through an interaction region perpendicular to the path of a fixed-frequency, cw argon ion laser operating at 351 nm. Electrons detached within a small solid angle are energy selected in a hemispherical electron energy analyzer before striking a position sensitive detector. Typical electron energy resolution is 6 meV. The electron kinetic energy scale is calibrated to the atomic oxygen electron affinity,[59] and a small correction for the energy scale compression is made using the known tungsten atom electron affinity and term energies.[60] The electron binding energy used throughout this paper is obtained by subtracting the electron kinetic energy from the photon energy (3.5311 eV).

Photoelectron angular distributions can be measured by rotating a half wave plate in the laser beam path, thereby rotating the polarization of the laser relative to the electron collection direction. The intensity of photoelectron detachment at a given photoelectron kinetic energy is dependent on the angle θ between the laser electric field polarization and the electron collection direction according to the equation,[61-63] $I_\theta \propto 1 - \beta P_2(\cos\theta)$, where $P_2(\cos\theta) = (3\cos^2\theta - 1)/2$, and β is the anisotropy parameter which can take values between -1 and $+2$, depending on the angular momentum possessed by the detached photoelectron. For atomic ions, detachment from an s orbital results in p-wave electrons ($\cos^2\theta$ distribution), so $\beta = +2$. Detachment from a p orbital results in a mixture of s- and d-wave electrons dependent on detachment energy above threshold: at threshold, pure s-wave detachment occurs and $\beta = 0$ (isotropic). As d-wave detachment mixes in at increasing electron energies β approaches -1 ($\sin^2\theta$ distribution) and then increases.[64] Though for molecular detachment the angular distribution is more complicated than for atomic detachment, we have found that, in general, β is positive for detachment from s-like orbitals and $\beta < 0$ for p-like orbital detachment.

The resolution of the Wien mass filter is $m/\Delta m \approx 30$, which means that at the mass of the isomers studied here (91 amu), the mass peak could be a convolution of ions within 2 amu of the desired mass. The identity of the signal carrier must therefore be carefully confirmed by ensuring clean source conditions, reaction with only one ion to produce a well-defined product, and, where possible, comparison with a photoelectron spectrum of an ion at a similar mass which is already well-known. Though the benzyl anion spectrum obscures part of the photoelectron spectrum of the other $C_7H_7^-$ isomers, it has proven to be a valuable confirmation of the mass of the selected ions. The benzyl spectrum is well-known, has a large photodetachment cross section, and obscures only *ca.* 0.4 eV of the spectral range. In addition, the photoelectron spectra of the $C_7H_7^-$ isomers, with the exception of quadricyclanide, do not have major features in the same binding energy range as benzyl anion, making use of benzyl anion as a mass confirmation especially advantageous.

Ion Formation. The ions were formed by reaction of a commercially available isomer of C_7H_8 (Aldrich, used as received) with a strong base (OH^- or NH_2^-) in the microwave-excited flowing afterglow source. The ion source consists of a 1 in. diameter glass tube surrounded by a microwave cavity through which helium (*ca.* 6 standard L per min) and, when required, trace amounts of O_2 are flowed. The tube feeds into the end of a 1.75 in. diameter, 18 in. long flow tube in which two reactant gas inlets can slide up and down the entire length.

---

(35) Lichtenberger, D. L.; Subramanian, L.; Bunz, U.; Vollhardt, K. P. C. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1351.

(36) Nagy-Felsobuki, E.; Peel, J. B.; Willett, G. D. *Chem. Phys. Lett.* **1979**, *68*, 523.

(37) Ervin, K. M.; Lineberger, W. C. *J. Phys. Chem.* **1991**, *95*, 1167.

(38) Haines, J.; Gilson, D. F. R. *Phase Trans.* **1990**, *21*, 1.

(39) Kubozono, Y.; Miyamoto, T.; Aoyagi, M.; Ata, M.; Matsuda, Y.; Gondo, Y.; Nakamura, H.; Matsuo, T. *Chem. Phys.* **1992**, *160*, 421.

(40) Reid, P. J.; Wickham, S. D.; Mathies, R. A. *J. Phys. Chem.* **1992**, *96*, 5720.

(41) Reid, P. J.; Lawless, M. K.; Wickham, S. D.; Mathies, R. A. *J. Phys. Chem.* **1994**, *98*, 5597.

(42) Srinivasan, R. *J. Am. Chem. Soc.* **1962**, *84*, 3432.

(43) Astholz, D. C.; Troe, J.; Wieters, W. *J. Chem. Phys.* **1979**, *70*, 5107.

(44) Troe, J.; Wieters, W. *J. Chem. Phys.* **1979**, *71*, 3931.

(45) Hippler, H.; Troe, J.; Wendelken, H. J. *Chem. Phys. Lett.* **1981**, *84*, 257.

(46) Hippler, H.; Troe, J.; Wendelken, H. J. *J. Chem. Phys.* **1983**, *78*, 5351.

(47) Hippler, H.; Shubert, V.; Troe, J.; Wendelken, H. J. *Chem. Phys. Lett.* **1981**, *84*, 253.

(48) Hippler, H.; Riehn, C.; Troe, J.; Weitzel, K.-M. *J. Phys. Chem.* **1990**, *94*, 6321.

(49) Jackson, R. L. *Chem. Phys.* **1991**, *157*, 315.

(50) Ikeda, N.; Nakashima, N.; Yoshihara, K. *J. Chem. Phys.* **1985**, *82*, 5285.

(51) Löhmannsröben, H.-G.; Luther, K. *Z. Phys. Chem. Neue Folge* **1986**, *149*, 129.

(52) Tsukiyama, K.; Bersohn, R. *J. Chem. Phys.* **1987**, *86*, 745.

(53) Borell, P. M.; Löhmannsröben, H.-G.; Luther, K. *Chem. Phys. Lett.* **1987**, *136*, 371.

(54) Bensimon, M.; Gaumann, T.; Zhao, G. *Int. J. Mass Spec. Ion Proc.* **1990**, *100*, 595.

(55) Huang, F.-S.; Dunbar, R. C. *Int. J. Mass Spec. Ion Proc.* **1991**, *109*, 151.

(56) Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Chem. Phys.* **1989**, *91*, 5974.

(57) Leopold, D. G.; Murray, K. K.; Stevens-Miller, A. E.; Lineberger, W. C. *J. Chem. Phys.* **1985**, *83*, 4849.

(58) Ervin, K. M.; Lineberger, W. C. *Advances in Gas Phase Ion Chemistry Vol. 1*; Adams, N. G., Babcock, L. M., Eds.; JAI Press: Greenwich, 1992; p 121.

(59) Neumark, D. M.; Lykke, K. R.; Andersen, T.; Lineberger, W. C. *Phys. Rev. A* **1985**, *32*, 1890.

(60) Moore, C. E. *Atomic Energy Levels*; U.S. GPO Circular No. 467: Washington, 1952.

(61) Cooper, J.; Zare, R. N. *J. Chem. Phys.* **1968**, *48*, 942.

(62) Cooper, J.; Zare, R. N. *J. Chem. Phys.* **1968**, *49*, 4252.

(63) Hall, J. L.; Siegel, M. W. *J. Chem. Phys.* **1968**, *48*, 943.

(64) Hanstorp, D.; Bengtsson, C.; Larson, D. J. *Phys. Rev. A* **1989**, *40*, 670.

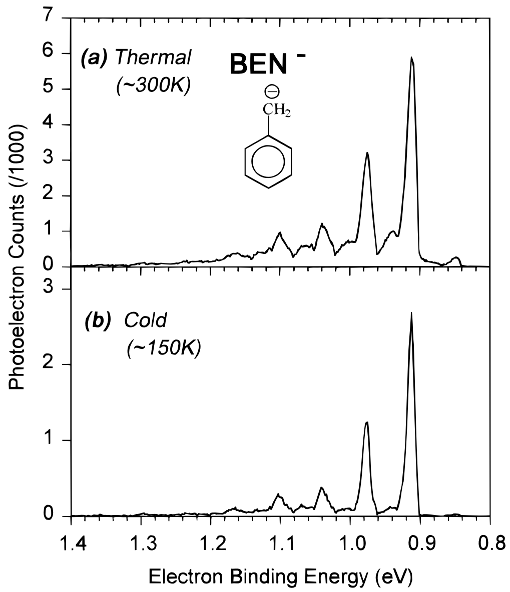

Figure 2. The 351 nm photoelectron spectrum of benzyl anion (BEN^-) produced by the reaction of toluene with OH^-. The spectrum was obtained with the ion source flow tube (a) at room temperature (for anion temperatures of 300(50) K) and (b) cooled with liquid nitrogen to produce anions at 150(50) K. See ref 1 for a detailed analysis of the room temperature spectrum.

The pressure in the flow tube is typically 0.5 Torr, and the gas is predominantly helium. The plasma formed by the microwave discharge extends all the way down the flow tube, at the end of which is a 1 mm diameter aperture through which the ions are extracted into a differentially pumped region. Under typical operating conditions the ion beam is monitored at the end of the spectrometer and the gas flows and inlet positions optimized to maximize the ion current. Hydroxide anions are formed by passing oxygen gas directly through the microwave discharge to make atomic oxygen anions and then introducing methane through one of the downstream inlets to form OH^-. Hydroxide ion currents are typically around 2 nA. Alternatively, ammonia can be used in place of oxygen gas to form amide anions, with typical beams of 200 pA. Formation of norbornadienide and quadricyclanide was implemented through eq 1 while benzyl anion, cycloheptatrienide, and 1,6-heptadiynide were formed by eq 2. The conditions required for efficient formation of each ion from the corresponding precursors are described below.

$$C_7H_8 + NH_2^- \rightarrow C_7H_7^- + NH_3 \tag{1}$$

$$C_7H_8 + OH^- \rightarrow C_7H_7^- + H_2O \tag{2}$$

Benzyl. The experimental conditions used to form benzyl anion from the reaction of toluene with OH^- have been described previously.[1] Although the conditions have not been changed dramatically from those used in the previous study, further optimization of the ion beam led to significantly greater currents than before (400 pA vs 15 pA), which leads to a photoelectron spectrum with significantly better signal-to-noise ratio (Figure 2a). Cooling the flow tube with liquid nitrogen cools the ions significantly while attenuating the ion beam only slightly. The cold spectrum in Figure 2b, obtained with 300 pA of ions, is substantially less congested and better resolved than that reported earlier with room temperature ions.

Quadricyclane. The reaction of quadricyclane with OH^- produced 9 pA of an ion at mass 91 amu. The photoelectron spectrum of this ion proved to be essentially identical to that of benzyl anion. The reaction reaction of with NH_2^-, a stronger base, leads to formation of 70 pA of ions at 91 amu and the photoelectron spectrum (Figure 3) contains only minimal signal from benzyl, with the remainder assigned to a quadricyclane-derived ion. As described in the accompanying paper (*J. Am. Chem. Soc.* **1996**, *118*, 5068),[2] hydroxide ion deprotonates toluene readily, but the reaction to deprotonate quadricyclane is endothermic. The presence of any toluene impurities in the quadricyclane sample, therefore, results in an efficient reaction to form benzyl anions. However, amide deprotonates quadricyclane efficiently enough to minimize spectral contamination by benzyl anion. The spectrum in Figure 3 represents the highest obtainable ratio of quadricyclanide to benzyl anions in the ion source of the photoelectron spectrometer.

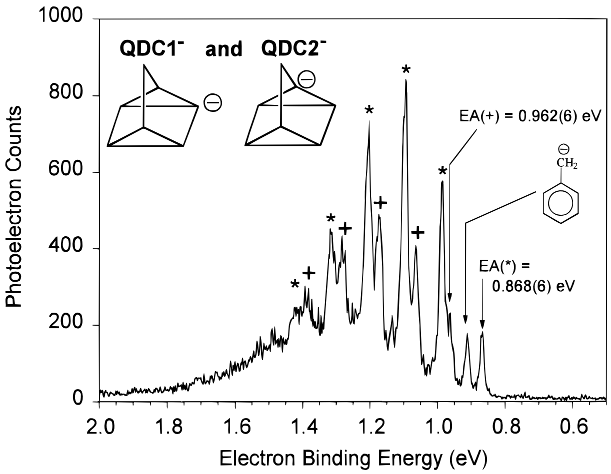

Figure 3. The 351 nm photoelectron spectrum of quadricyclanide anions ($QDC1^-$ and $QDC2^-$), obtained with the laser polarization oriented parallel to the electron collection direction to minimize contamination by benzyl anion. The origin of the benzyl anion contaminant signal is indicated, and the peaks tentatively assigned to the spectra of two QDC^- isomers are indicated with * and + symbols. The experimental data do not permit the identification of one set of peaks (* or +) with a particular isomer ($QDC1^\bullet$ or $QDC2^\bullet$); ab initio calculations[2,16] suggest that $QDC1^\bullet$ has the lower EA (isomer "*").

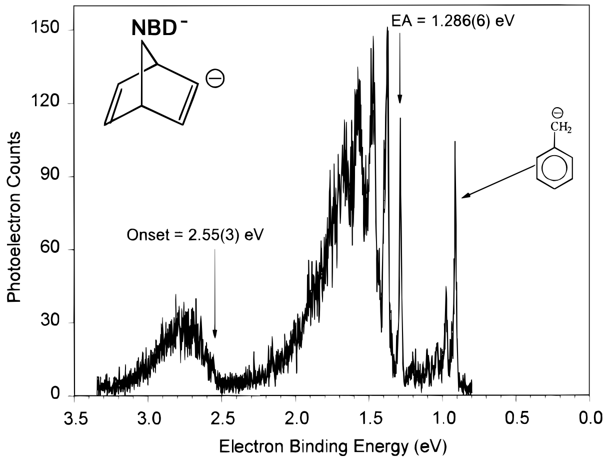

Figure 4. The 351 nm photoelectron spectrum of norbornadienide anion (NBD^-). The origin of the benzyl anion contaminant signal is indicated, as are the peaks resulting from transitions to the vibrationless origins of the ground and first excited states of $NBD^\bullet$.

Norbornadienide. Amide ions were used to deprotonate norbornadiene. A 120 pA beam of ions was obtained at mass 91 amu, giving the spectrum shown in Figure 4. The photoelectron spectrum of benzyl anion also appears as a contaminant in Figure 4. The norbornadiene sample was confirmed to be contaminated with toluene (<1%) using GC/MS, and the benzyl signal is probably entirely due to this contamination.

1,6-Heptadiynide. The reaction of hydroxide with 1,6-heptadiyne produced large (600 pA) ion currents of the deprotonated molecule. Spectra were recorded with the flow of 1,6-heptadiyne attenuated until the ion beam was 150−200 pA to minimize spectral complications due to space-charge degradation of the electron energy resolution in the photoelectron spectrometer. The photoelectron spectrum suggests the possibility that two isomers (with a low and high electron binding energy) are produced in the ion source. The presence of two isomers was confirmed by moving the 1,6-heptadiyne inlet forward and back in the source flow tube and altering the helium flow. Introduction of

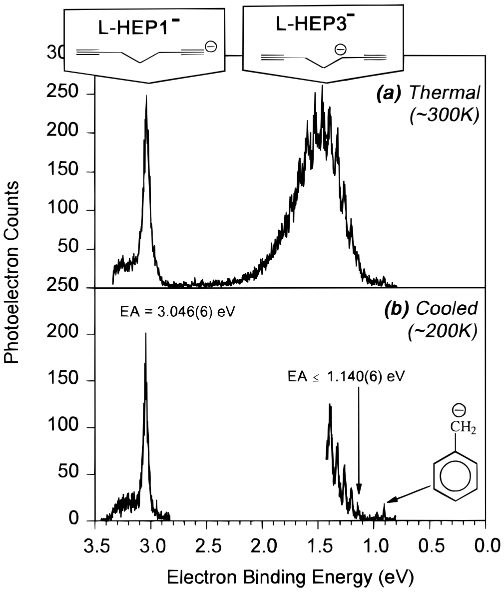

Figure 5. The 351 nm photoelectron spectrum of 1,6-heptadiynide anion (L-HEP1⁻ and L-HEP3⁻). Shown are (a) the spectrum obtained from ions formed at approximately room temperature (300(50) K) and (b) portions of the spectrum resulting from cooling the source with liquid nitrogen to produce anions at 150(50) K. Transitions to the ground states of the two isomers L-HEP1• (end hydrogen removed) and L-HEP3• (hydrogen removed from C_3) are labeled.

the 1,6-heptadiyne near the ion source slightly favored production of the more strongly bound ion. Spectra were also recorded while mass selecting slightly higher and lower portions of the mass peak to confirm that both electronic states in Figure 5 result from detachment from the same mass species.

Cycloheptatrienide. The reaction of OH^- with cycloheptatriene resulted in 220 pA of ions at 91 amu, while the reaction with NH_2^- produced 100 pA of ions at the same mass. The photoelectron spectra obtained with the two reactions are shown in Figure 6. The relative intensities of the three features marked A, B, and C in Figure 6 are dependent on source conditions and reactants, and the factors which govern these intensities will be discussed below. The sample of cycloheptatriene contained toluene (<1%), according to a GC/MS analysis, and the spectrum of benzyl anion is very prominent in the CHT^- spectrum as a result. However, no major features of the cycloheptatrienide spectrum are obscured by the benzyl anion contaminant.

Results and Discussion

The photoelectron spectra to be discussed below are shown in Figures 2 (BEN^-), 3 ($QDC1^-$ and $QDC2^-$), 4 (NBD^-), 5 (L-HEP1⁻ and L-HEP3⁻), and 6 (CHT^-). The molecular properties obtained by analysis of the spectra are summarized in Table 1. Each spectrum is described and analyzed in turn below.

Benzyl Spectrum. The benzyl anion spectrum is shown in Figure 2 for electron binding energies between 0.8 and 1.4 eV, which contains all the features of the spectrum. Figure 2a contains the spectrum obtained from ions produced by a room temperature flow tube, where the anion temperature is estimated to be 300(50) K. A similar spectrum has been presented previously and analyzed in detail.[1] The spectrum in Figure 2b was obtained with the flow tube cooled by liquid nitrogen. A Franck−Condon analysis of this spectrum provides an estimated anion temperature of 150(50) K.

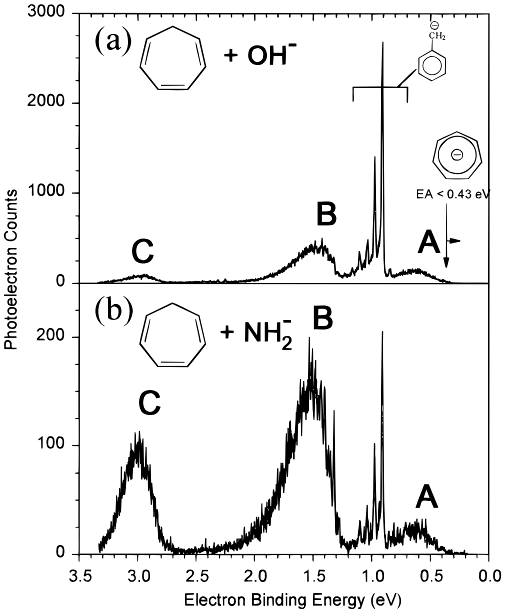

Figure 6. The 351 nm photoelectron spectrum of anions at mass 91 amu generated from the reaction of cycloheptatriene with (a) hydroxide and (b) amide. Band A is assigned to transitions to the ground state of the indicated isomer of CHT•, for which the approximate electron affinity is indicated. Bands B and C are assigned as transitions to the ground and first excited electronic states of one or more of other isomers of $C_7H_7^-$, most likely linear vinyl anions from ring-opening of the cycloheptatriene ring in the ion source region.

Quadricyclanide Spectrum. The spectrum of quadricyclanide, obtained by reaction of quadricyclane with amide ion, is shown in Figure 3 for electron binding energies from 0.5 to 2.0 eV. The remainder of the spectrum does not contain any additional features and is not shown. The spectrum in Figure 3 was obtained with the laser polarization parallel to the electron collection direction to minimize contamination due to photodetachment from benzyl anion. No excited states of the neutral are apparent in the photoelectron spectrum, and the peaks are well separated for up to *ca.* 0.5 eV of internal energy (1.3 eV total electron binding energy), indicating the presence of at least one vibrational progression with a harmonic frequency of approximately 900 cm^{-1}. On closer inspection, one peak can be assigned as the origin of the benzyl anion spectrum (indicated in Figure 3), and, though the origin peak at 0.868 eV binding energy is a single peak, the peaks at 0.962 eV binding energy and higher which form the main progression appear to be grouped in pairs consisting of a large peak with a smaller companion at lower binding energy.

The presence of the second series of peaks can result from several causes: (1) hot band transitions from $v = 1$ of the anion giving rise to a series of vibrations in the neutral, (2) two nearly degenerate vibrations in neutral quadricyclenyl may be active upon photoelectron detachment, or (3) the two sets of peaks may result from transitions to two electronic states of the neutral. The first possibility is highly unlikely, because it would require nearly equal populations in the anion $v = 1$ and $v = 0$ levels, implying anion temperatures on the order of 1000 K, inconsistent with the thermal conditions typical for the flowing afterglow source. The second possibility was tested by performing a Franck−Condon analysis where the spectrum was modeled as two vibrations in one electronic state. This analysis produced significantly greater spectral congestion than is present in the spectrum, due to the presence of combination bands required by the independent harmonic oscillator approximation.

The only remaining possibility, that two electronic states are present, requires either that QDC• has two electronic states separated by only 760 cm^{-1} (the spacing between the two origins), or that two quadricyclanide anions are formed upon deprotonation of quadricyclane. The first excited state of the

Table 1. Experimental Constants of C_7H_7 Radicals Determined from the 351 nm Photoelectron Spectra (Figures 2−6) of the $C_7H_7^-$ Isomers Depicted in Figure 1 and of Benzyl Anion

C_7H_7 isomer	EA (eV)	VDE (eV)	term energy (eV)	obsd vibration(s) (cm^{-1})	normal coordinate displacement ($(g/mol)^{1/2} * Å$)	anisotropy parameter, β, measured at eKE[a]
QDC1$^\bullet$/QDC2$^\bullet$ [b]						
isomer "*"	0.868(6)		0	909(20)	0.46	+0.6(2) @ 2.663 eV
isomer "+"	0.962(6)		0	826(20)	0.43	+0.5(2) @ 2.569
NBD$^\bullet$						
ground state	1.286(6)		0	710(20)	0.40	+0.9(1) @ 2.245
				800(30)	0.32	
				1150(20)	0.20	
excited state		2.8(1)	1.26(3)	350(150)		−0.1(5) @ 0.73
L-HEP3$^\bullet$	1.140(6)	1.5(1)	0	500(20)		−0.3(1) @ 1.53
L-HEP1$^\bullet$	3.046(6)	3.037(6)	0			+0.5(1) @ 0.5
CHT$^\bullet$ [c]						
feature A	0.39(4)	0.64(10)	0			−0.2(1) @ 2.89
feature B	1.32(2)	1.48(10)	0			−0.1(1) @ 2.05
feature C		2.97(10)	1.65(10)			+0.3(1) @ 0.56
BEN$^\bullet$ (from ref 1)	0.912(6)		0	514(15)	0.28	−0.42(10) @ 2.619
				1510(25)	0.08	

[a] Electron kinetic energies at which the anisotropy parameters are measured, in eV. [b] Ab initio calculations[2,16] suggest that QDC1$^\bullet$ is the lower EA species (isomer "*"); however, the spectral data do not contain enough information to make this assignment. [c] Spectrum derived from the cycloheptatriene reaction includes more than one anion. Numbers in the table are from the hydroxide reaction products (see text).

neutral is expected to lie several eV above the ground state, effectively ruling out the possibility of two states in one isomer. Data from H/D exchange experiments described in the accompanying paper (*J. Am. Chem. Soc.* **1996**, *118*, 5068)[2] are consistent with deprotonation at two sites on quadricyclane, implying that the two anions QDC1$^-$ and QDC2$^-$, depicted in Figure 1, are formed in the ion source. The gas-phase acidities of these two sites on quadricyclane are too similar to be distinguished in the SIFT apparatus,[2] however, and the bond dissociation energies have not been measured (and must be nearly equal as well, since the EAs of the radicals differ by only *ca.* 2 kcal/mol). Therefore, though the binding energies of the two isomers of the anion are well-defined, we cannot definitively assign one isomer as the lower binding energy species from the photoelectron spectra, and the assignments in Table 1 reflect this ambiguity. In two independent efforts to obtain a more firm assignment, Lee[2] and Karney[16] have recently calculated the EAs of QDC1$^\bullet$ and QDC2$^\bullet$. Both calculations predict that QDC1$^\bullet$ has the lower electron affinity. Further information concerning the thermochemistry of quadricyclane is included in the accompanying paper (*J. Am. Chem. Soc.* **1996**, *118*, 5068).[2]

Norbornadienide Spectrum. The norbornadienide spectrum in Figure 4 contains, in addition to the BEN$^-$ signal, two major features centered at 1.6 and 2.8 eV binding energy. The feature at lower binding energy, which corresponds to transitions to the ground electronic state of NBD$^\bullet$, has several well-resolved peaks including the origin at 1.286(6) eV binding energy. The remaining peaks are at higher binding energy than the origin and result from transitions to higher vibrations of the NBD$^\bullet$ ground state. A Franck−Condon simulation of this electronic state shows that three vibrational modes are active at 710(20), 860(30), and 1150(20) cm^{-1}. The normal coordinate displacements of these modes are included in Table 1. The spectral feature centered at 2.8 eV corresponds to transitions to an excited electronic state of NBD$^\bullet$. The origin of this state appears at 2.55(3) eV, and a vibrational feature can be seen at 350(150) cm^{-1} above the origin. The large error bar assigned to the origin is a result of congestion which renders the vibrational structure almost unresolvable.

Angular distributions have been measured for both electronic states and provide important information about the symmetries of the orbitals from which the electrons are ejected in each case. The anisotropy parameter, β, is measured to be +0.9(1) and −0.1(5) for the ground and excited states of norbornadienyl, respectively. The positive anisotropy parameter for the ground state is consistent with what is expected for σ orbital detachment, confirming that the photoelectron is detached from the σ lone pair formed at the deprotonated carbon atom. The excited state has a nearly isotropic angular distribution, likely due to detachment from the π system.

The presence of a low-lying excited state of phenyl and vinyl radicals has been noted previously in the photoelectron spectra of phenyl anion[1] and 3,3-dimethylcyclopropenide.[65] These ions are similar to NBD$^-$ in that they contain two electrons in an sp^2 orbital on a dehydrocarbon. Excited states are observed in the photoelectron spectra of these two ions, with characteristics, such as anisotropy parameters, similar to those observed for NBD$^-$. These electronic states are <1.7 and 1.37 ± 0.02 eV higher than the ground states of phenyl[1] and dimethylcyclopropenyl[65] radicals, respectively. For comparison, the excitation energy of the excited state of NBD$^-$ is 1.26 ± 0.03 eV. Electronically, these states consist of two electrons in a nonbonding σ orbital and have one electron in a bonding π-orbital. Such an electronic state can be formed via a spin-conserving π-σ transition in the ground state radical. The energy required for such a transition is low, on the order of 25 kcal/mol.

Several efforts have been made to elucidate the relative importance of through-bond vs through-space interactions of the π bonds in norbornadiene. The consensus[22−27] has been that through-space interactions are dominant. It is possible that these interactions could affect the energy of the π bond in NBD$^\bullet$, which would change the energy of the excited state. However, the excited state energy in NBD$^\bullet$ is similar to that of dimethylcyclopropenyl radical, in which there is only one π bond from which to detach the electron, which indicates either that the presence of the second π bond does not significantly influence the relative energy of the π system in NBD$^\bullet$ as compared to 3,3-dimethylcyclopropenyl radical or that the effects are offset by a comparable amount.

1,6-Heptadiynide Spectrum. Unlike the cases of quadricyclane, norbornadiene, and cycloheptatriene, no flowing afterglow studies have been published about the gas-phase reactivity

---

(65) Gunion, R. F.; Kass, S. R.; Lineberger, W. C., unpublished results.

of 1,6-heptadiyne with a strong base. Therefore, the position from which the proton is removed from 1,6-heptadiyne has not been experimentally determined. Removal of a proton from the end of the molecule results in an acetylenic anion (L-HEP1$^-$ in Figure 1), where the negative charge is stabilized by its proximity to the C≡C bond. The photoelectron spectrum of such an anion is expected to be similar to that[37] of C_2H^-, where the electron affinity of the neutral is 2.969 eV and the geometry change between the anion and neutral is very small. Alternatively, proton abstraction from C_3 will result in an anion similar to allenyl (e.g., L-HEP3$^-$ in Figure 1). In this case the photoelectron spectrum should appear similar to that of allenyl anion,[3] which has an origin at 0.918 eV (the EA of propargyl radical) and a highly extended vibrational progression in a 470 cm^{-1} mode. Proton abstraction from C_4 of 1,6-heptadiyne is not expected to proceed efficiently since the resulting anion is not stabilized by an allenyl or acetylenic interaction of the carbon chain with the negative charge. Deprotonation of 1,6-heptadiyne, therefore, is expected to produce at least one of the L-HEP$^-$ isomers depicted in Figure 1, and the photoelectron spectra of these isomers should be easily distinguishable from one another.

Figure 5 depicts the photoelectron spectra obtained for deprotonated 1,6-heptadiyne with the ion source flow tube at room temperature (Figure 5a) and cooled with liquid nitrogen (Figure 5b), resulting in anion temperatures of 300(50) K and 200(100) K, respectively. The spectra contain two electronic states, centered around *ca.* 1.5 and 3.0 eV binding energies. The origin of the benzyl anion spectrum appears in Figure 5b, confirming the mass of the signal carrier. The low binding energy state is broad and appears characteristic of a transition involving a large normal coordinate displacement in at least one vibrational mode. In this case, individual vibrational peaks are regularly spaced by 500(20) cm^{-1}. Conversely, the electronic state at 3.0 eV binding energy appears much sharper, as expected for a transition with a small geometry change. These observations are consistent with what is expected for formation of both L-HEP$^-$ isomers, as described above.

The angular distributions for photodetachment to the states in Figure 5 were also measured. The measured anisotropy parameters for the high- and low-binding energy states are $\beta = +0.5(1)$ (σ-orbital detachment) and $-0.3(1)$ (π-orbital detachment), respectively. These values further confirm the isomeric identities of the signal carriers for the spectra: the acetylenic anion (L-HEP1$^-$) detaches an electron from a lone pair with σ-like symmetry, similar to the C_2H^- case, resulting in a positive anisotropy parameter. In the case of L-HEP3$^-$, the electron is detached from a π-type orbital which arises from a resonance structure. Using the angular distribution measurements in addition to comparisons with the allenyl and C_2H^- photoelectron spectra, the electronic states appearing at high and low binding energies in Figure 5 are firmly assigned to transitions from L-HEP1$^-$ and L-HEP3$^-$, respectively.

The high binding energy peak, which corresponds to the L-HEP1$^-$ photoelectron spectrum, is centered at 3.046(6) eV in the cold spectrum (Figure 5b). This position corresponds to the EA of L-HEP1$^•$. A smaller, more diffuse feature at higher binding energy probably results from a small displacement in at least one vibrational mode. However, this peak is too diffuse to extract a vibrational frequency.

Comparison of the room temperature spectrum with the cold spectrum in the 0.8 to 1.4 eV binding energy region reveals that much of the spectral congestion is removed by cooling, and, as a result at least one vibrational peak at 1.140(6) eV is apparent in the cold spectrum that cannot be resolved in the room temperature spectrum. This peak is the last clearly visible peak in the cold spectrum, placing an upper limit on the origin of this electronic state. However, it could be a transition to an excited vibrational level of the neutral. In this case the vibrationless origin would have a Franck–Condon overlap too small to appear in the photoelectron spectrum. The peak location, therefore, can only provide an upper bound to the EA, such that EA(L-HEP3$^•$) $\leq$ 1.140(6) eV.

The similarity between the L-HEP1$^-$ and L-HEP3$^-$ photoelectron spectra and those[3,37] of C_2H^- and H_2CCCH^-, respectively, is remarkable considering the findings of a photoelectron study[35] of 1,6-heptadiyne itself. In that study, the photoelectron spectrum of 1,6-heptadiyne was broadened by the presence of two electronic states, corresponding to two conformers of the molecule with significantly different energies. The origin of the broadening was investigated in light of through-space versus through-bond interactions between the acetylene groups. The through-space interactions were found to be negligible while the through-bond interactions were found to be extensive. These findings imply that extensive mixing between the π and the σ orbitals of the carbon framework exists. The orbitals might be expected, therefore, to behave similarly in the deprotonated anion, altering the photoelectron spectra of L-HEP1$^-$ and L-HEP3$^-$ relative to those of C_2H^- and H_2CCCH^-. The appearances of the analogous spectra are almost identical, however, in terms of electron affinities, normal coordinate displacements, and even the frequency of the active vibrational mode in the L-HEP3$^-$ spectrum (500(20) cm^{-1}, compared to 470 cm^{-1} in the allenyl spectrum). Aside from a very slight increase in the electron binding energy, the only apparent difference between the analogous spectra is the anisotropy parameter: the angular distributions of photodetachment from L-HEP1$^-$ and L-HEP3$^-$ are much more isotropic than the C_2H^- and allenyl spectra. While this is indicative of significant mixing between the σ and π bonds, the lack of changes in other aspects of the spectra is surprising. Apparently, the spectra are only affected in subtle ways by the mixing of the π orbitals with the σ orbitals. The dominant factor determining the appearance of photoelectron spectra is the nature of the orbital from which the electron is detached, rather than the presence of functional groups elsewhere in the molecule. This effect has been explored[66] in the past in this laboratory and will be the subject of future investigations.

Cycloheptatrienide Spectrum. The photoelectron spectra of the 91 amu products of the reaction of cycloheptatriene with OH^- and NH_2^- are shown in Figure 6. The benzyl spectrum is very prominent in this case, probably due to greater contamination of the cycloheptatriene sample by toluene than of the other samples. Three features, marked A, B, and C, appear in Figure 6 which are attributable to photodetachment from one or more products of the CHT$^-$ reaction. At least three products make up these features, as discussed below, and all appear at 91 amu in the mass spectrum, as confirmed by obtaining photoelectron spectra on the high and low mass sides of the ion mass peak.

Spectra were recorded for the products of the hydroxide reaction with cycloheptatriene under varying ion source conditions to help characterize the identities of the 91 amu ions. In the hydroxide reaction, features B and C remain at the same relative intensities regardless of source conditions, indicating that they result from photodetachment of a single anion to form two electronic states of the neutral. In contrast, feature A is attenuated relative to B and C when the cycloheptatriene inlet

---

(66) Gunion, R. F.; Köppel, H.; Leach, G. W.; Lineberger, W. C. *J. Chem. Phys.* **1995**, *103*, 1250.

is placed near the beginning of the flow tube. Whether the attenuation of feature A is due to longer reaction times in the flow tube or to the relative proximity of the inlet to the microwave plasma is unclear. However, either condition shows that the ion is relatively fragile. The reaction of hydroxide with cycloheptatriene then produces two distinct anions at mass 91 amu, one of which has a low binding energy (indicated by the low binding energy of feature A) and is easily destroyed, while the other has a binding energy of nearly 1 eV and two electronic states accessible to the 3.5 eV photon energy of the spectrometer.

The photoelectron spectrum associated with the mass 91 amu products of the cycloheptatriene reaction with amide is similar to the hydroxide reaction products, except for three significant differences: (1) the intensity of feature C is greater relative to feature B than in the hydroxide reaction, (2) additional, sharp peaks appear in feature B which are not apparent in the hydroxide spectrum, and (3) the ratio of the intensity of feature B to that of the benzyl signal is close to 1:1, as compared to 1:6 from the hydroxide reaction product. The first two differences indicate that at least one more ion at mass 91 amu is produced by the reaction with amide than by the hydroxide reaction and that the additional ion(s) produce photoelectron spectra similar to the single ion produced in the hydroxide reaction. The third indicates that the cycloheptatriene-derived anions which correspond to features A, B, and C are produced more efficiently by the reaction with amide than by the hydroxide reaction.

The implications derived from the photoelectron spectra of the products of the cycloheptatriene reactions with amide and hydroxide encompass several possibilities for the identities of the signal carriers for features B and C. However, the findings of previous gas-phase reactivity studies[5] enable the unambiguous assignment of feature A to the isomer of CHT^- depicted in Figure 1. The product of the hydroxide reaction with cycloheptatriene has been identified by H/D exchange experiments, and the gas-phase acidity (375.2 ± 2.0 kcal/mol)[9] and C−H bond dissociation energy (73.4 ± 2.0 kcal/mol)[10] have been measured. From these two measurements and a thermochemical cycle $[\mathrm{EA(A)} = \mathrm{BDE(HA)} - \Delta H_{\mathrm{acid}}\mathrm{(HA)} + \mathrm{IP(H)}]$ the EA of cycloheptatriene is estimated[10] to be 11.8(4.0) kcal/mol. Although the vibrationless origin of feature A cannot be firmly identified, the typical temperatures of anions upon exiting the source region (300(50) K) imposes a maximum binding energy of the anion corresponding to feature A of 0.43 eV (9.9 kcal/mol), which is consistent with the above estimate. Combining our findings with the above estimate, the electron affinity of this species is 9 ± 1 kcal/mol (0.39 ± 0.04 eV). The binding energy of the anion(s) associated with feature B is *ca*. 1 eV, more than twice the previous estimate and therefore inconsistent with the CHT^- isomer represented in Figures 1 and 6.

The feature assigned to the CHT^- ion does not contain well resolved peaks. This is possibly due to the fact that there are many low-lying modes in $CHT^\bullet$, resulting in a potential energy surface corresponding to the ground state of $CHT^\bullet$ is fairly flat. Calculations at the MCSCF(7,7)/6-31G* and CASPT2N/6-31G* levels of theory predict that the $^2A_2$ and $^2B_1$ Jahn-Teller distorted states are the lowest energy states of $CHT^\bullet$ and are essentially equal in energy such that the barrier to pseudo-rotation is zero.[67] This suggests that $CHT^\bullet$ is a highly fluxional molecule, consistent with what is observed in the photoelectron spectrum.

Although the signal carrier for feature A is easily identified, features B and C have a more complicated origin. These features arise from at least two ions at mass 91 amu, since there relative intensities are dependent upon the source conditions. Detachment of either of these ions produces remarkably similar photoelectron spectra, and these photoelectron spectra must also be very similar to those of norbornadienide (Figure 4) and L-HEP3$^-$ (Figure 5), indicating that the electron is detached from similar environments in all of these cases. Three isomers of CHT^- may be accessible, corresponding to deprotonation of cycloheptatriene at the three distinct sites other than the methylene group. Each of these isomers leaves the electron next to a vinyl group, consistent with the positions and appearances of features B and C. Another possibility is that the ring of a $C_7H_7^-$ isomer derived from cycloheptatriene (deprotonated at any of the four distinct sites) opens to produce a linear ion. This possibility could produce a vinyl or allenyl ion, which would be consistent with the observed photoelectron spectrum, and the linear anion would likely have a much lower heat of formation relative to the CHT^- isomers. The similarity of the positions and appearance of features B and C to the photoelectron spectra of NBD^-, L-HEP3$^-$, and allenyl anions makes it very probable that the signal carriers are not impurities in the cycloheptatriene sample. Although none of the three possibilities can be ruled out completely, the ring-opening explanation is the most likely. This explanation is also supported by the observation that feature A is attenuated by moving the cycloheptatriene inlet to the beginning of the flow tube, since this is consistent with the ring opening of CHT^- by collisions with the buffer gas or by contact with the hotter plasma near the beginning of the flow tube. This interpretation would seem to be contradicted by the observation that the reaction of cycloheptatriene with hydroxide and amide seems to produce only one product (CHT^-) in a FA/SIFT apparatus.[68] However, while the ion source in that apparatus is designed to thermalize efficiently the reactants and products, the photoelectron spectrometer ion source was designed primarily to produce a large flux of ions, with less emphasis on controlled reaction conditions. Endothermic reactions have been observed before under our source conditions,[1] and such conditions seem to be necessary to induce ring-opening in cycloheptatriene.

The angular distributions were measured for features A, B, and C in the photoelectron spectrum of the hydroxide reaction products with cycloheptatriene. The measured anisotropy parameters are $\beta = -0.22$, -0.1, and $+0.32$ for states A, B, and C, respectively. These values indicate that detachment to form feature A comes from a π type orbital, although the magnitude is not as large as that for benzyl anion (-0.42). The valence electron in CHT^-, therefore, is apparently in an out-of-plane orbital but is not strongly aromatically coupled to the remaining out of plane orbitals (the three double bonds) as the out of plane orbital is on the benzyl anion. The electron which detaches to form the "B" state is nearly isotropic, indicating detachment from an orbital which, though primarily a π type orbital, contains significant σ character. The "C" state displays a positive anisotropy parameter, indicating that the electron detached in this case has mostly σ character.

Comparison of C_7H_7 Ions. From the photoelectron spectra and electron binding energies of the C_7H_7 anions examined in this study, certain conclusions regarding the nature of the ions can be made. First of all, the ordering of the electron binding energies for the ions is $CHT^- < QDC1^- \approx QDC2^- \approx BEN^- <$ L-HEP3$^- \approx NBD^- <$ L-HEP1$^-$. In general, this follows the expected trend that the ions with electrons in orbitals with more s-character will be more strongly bound. This accounts for the ordering of CHT^- (p orbital), $QDC1^-$ and $QDC2^-$ (sp^3), NBD^- (sp^2), and L-HEP1$^-$ (sp). The exceptions to this trend are BEN^- and L-HEP3$^-$.

---

[67] Hrovat, D. A.; Borden, W. T., unpublished results.

[68] Lee, H.-S.; Bierbaum, V. M.; DePuy, C. H., private communication.

Both of these ions have a pair of electrons in π orbitals, as indicated by the anisotropy parameters. In this way, they are like the CHT$^-$ ion. However, the binding energies of BEN$^-$ and L-HEP3$^-$ are significantly higher than that for CHT$^-$. This is due to the fact that the charge in BEN$^-$ and L-HEP3$^-$ is stabilized by delocalization. Delocalization in CHT$^-$ does not stabilize the ion significantly because an antiaromatic system would be created. Therefore, the binding energy of COT$^-$ is consistent with what is expected for an ion with electrons in a localized p-like orbital, consistent with the conclusion derived from the angular distribution studies.

Conclusions

The photoelectron spectra of several isomers of $C_7H_7^-$ have been presented, from which the electron affinities of the corresponding $C_7H_7^\bullet$ radicals have been measured. Deprotonation of quadricyclane can occur at two distinct sites which have measurably different electron affinities. Although the identification of one isomer as the more weakly bound species is difficult due to the similar gas phase acidities of the isomers, ab initio calculations[2,16] suggest that dehydrogenation at C_1 the radical with the lower EA. Norbornadiene deprotonates at only one site upon reaction with amide, and the photoelectron spectrum shows the ground and one excited state resulting from detachment from a σ and a π orbital, respectively. Deprotonation of 1,6-heptadiyne can occur at the end carbon to form an acetylide-like anion or at the third carbon to produce an anion similar to allenyl. The electron affinities of the 1,6-heptadiyne-derived radicals are dramatically different, and the photoelectron spectra are easily identifiable by comparison with the known[3,37] photoelectron spectra of C_2H^- and allenyl. The photoelectron spectra obtained by deprotonating cycloheptatriene with hydroxide and amide contain signal at low binding energy due to the isomer resulting from deprotonation at the methylene group, and at least two other isomers are formed which photodetach at higher binding energies. By comparison of the binding energy of the CHT$^-$ ion with those of the other ions in this study, it is concluded that the CHT$^-$ ion is best thought of as a localized, π-type anion. Although the identities of the additional isomers in the CHT$^-$ spectrum are not clearly identified, the resemblance of their photoelectron spectra to vinyl anions, the confirmation of their mass at 91 amu, and thermochemical considerations support the conclusion that they are linear forms of $C_7H_7^-$ resulting from the opening of the cycloheptatriene ring.

The photoelectron spectrum of benzyl anion ($C_7H_7^-$), which has been reported previously,[1] appears in the spectra of each of the other $C_7H_7^-$ isomers. Tests for contamination of the norbornadiene and cycloheptatriene samples by toluene proved positive, while a similar test for toluene in the quadricyclane sample was inconclusive. The benzyl anion spectrum probably results from contamination of the samples by toluene, therefore, rather than from an isomerization during or after deprotonation.

This investigation has produced extensive new information about the C_7H_7 radicals and anions derived from reaction of quadricyclane, norbornadiene, 1,6-heptadiyne, and cycloheptatriene with strong bases (OH^- or NH_2^-). The complexity of the systems raises many questions, and while several have been answered, many still remain or have been raised anew by this study. This work illustrates further the difficulties in separating the properties of the many isomers on the $C_7H_7^-$, $C_7H_7^\bullet$, and C_7H_8 potential energy surfaces. The combination of negative ion photoelectron spectroscopy with the FA/SIFT technique has proven to be one of the most promising avenues available in such a pursuit.

Acknowledgment. This work was supported by National Science Foundation Grants No. PHY90-12244 and CHE93-18639. We thank Prof. Charles H. DePuy, Prof. Veronica M. Bierbaum, and Dr. Hack-Sung Lee for an enjoyable and fruitful collaboration, and Prof. G. Barney Ellison for many stimulating conversations.

JA954026F