(15) P. J. Wagner and D. J. Bucheck, *J. Am. Chem. Soc.*, **91**, 5090 (1969).
(16) The self-quenching is a special case of the olefin–enone interaction, and may likewise pass through a reversibly formed triplet complex. The *true* value of K_{sq}, if there should be reversion to triplet, is not available from the presently available results.[15] The experiments at low temperature, in which reversion should be decreased, suggest the latter is not important.
(17) See, for instance, O. L. Chapman and R. D. Lura, *J. Am. Chem. Soc.*, **92**, 6352 (1970); W. R. Ware, D. Watt, and J. D. Holmes, *ibid.*, **96**, 7853 (1974); H. Nakashima, N. Mataga, and C. Yamanaka, *Int. J. Chem. Kinet.*, **5**, 833 (1973); H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 839 (1969); D. Creed, P. H. Wine, R. A. Caldwell, and L. A. Melton, *J. Am. Chem. Soc.*, **98**, 622 (1976).
(18) For a recent example, see J. J. McCullough, B. R. Ramachedran, F. F. Snyder, and G. N. Taylor, *J. Am. Chem. Soc.*, **97**, 6767 (1975). For a general discussion of triplet exciplexes and reversibility see: D. G. Whitten in "The

Exciplex", M. Gordon and W. R. Ware, Ed., Academic Press, New York, N.Y., 1975, p 247.
(19) R. A. Caldwell, G. W. Sovocol, and R. J. Gajewski, *J. Am. Chem. Soc.*, **95**, 2549 (1973).
(20) P. J. Wagner and I. Kochevar, *J. Am. Chem. Soc.*, **90**, 2232 (1968).
(21) A. Gupta and G. S. Hammond, *J. Am. Chem. Soc.*, **98**, 1218 (1976).
(22) A. Devaquet and L. Salem, *Can. J. Chem.*, **49**, 977 (1971), and A. Devaquet, *J. Am. Chem. Soc.*, **94**, 5160 (1972).
(23) Margaretha has made similar conclusions with 3-oxaenones on the basis of an excessively simplified kinetic scheme: P. Margaretha, *Chimia*, **29**, 703 (1975). This has been modified in later papers: G. V. Thi and P. Margaretha, *Helv. Chim. Acta*, **59**, 2236 (1976).
(24) W. L. Dilling, T. E. Tabor, F. P. Boer, and P. D. North, *J. Am. Chem. Soc.*, **92**, 1399 (1970).
(25) K. Wiesner, *Tetrahedron*, **31**, 1655 (1975).
(26) P. G. Bauslaugh, *Synthesis*, **2**, 287 (1970).

Electron Photodetachment from Negative Ions of C_{2v} Symmetry. Electron Affinities of Allyl and Cyanomethyl Radicals

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Abstract: The cross sections for electron photodetachment from allyl and cyanomethyl anions have been measured. The threshold behavior of these cross sections is shown to be in agreement with that predicted by symmetry from molecular orbital theory. The cross sections at threshold are calculated assuming molecular orbital initial states for the ions and a plane wave final state for the detached electron. The electron affinities of allyl radical (0.550 ± 0.054 eV) and cyanomethyl radical (1.507 ± 0.018 eV) are determined by fitting the calculated cross sections to the experimental data. An estimate is made of the resonance energy of the allyl anion.

Photodetachment spectroscopy is becoming one of the most commonly employed methods for obtaining accurate electron affinities. Extracting electron affinities from photodetachment data is straightforward for atoms.[1–3] However, for diatomic and polyatomic molecules the photodetachment data become a complicated function of rotational,[4] vibrational,[5,6] and occasionally electronic transitions,[7] each transition having in general some complicated dependence on the photoelectron energy. This process is

$$A^-(J,v) + \hbar\omega \rightarrow A(J',v') + e^-(E_k) \tag{1}$$
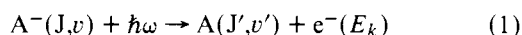
where J and J' are initial and final rotational states, v and v' are initial and final vibrational states, and E_k is the energy (momentum k) of the photoelectron.

When only a single vibrational transition is involved ($v = v'$), interpretation of photodetachment data is straightforward provided the dependence of the cross section on photoelectron energy is known. This dependence is determined to first order at threshold by the symmetry of the anion and the symmetry of the orbital from which the electron is detached.[8] The photodetachment threshold behavior can thus provide information on orbitals and their symmetry in anions.[8]

In this paper we present the photodetachment spectra of two anions possessing C_{2v} symmetry: allyl anion, **1**, and cyanomethyl anion, **2**. The highest occupied molecular orbital


1

2
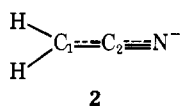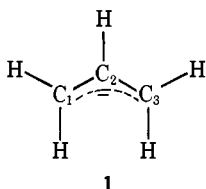
(HOMO) of allyl anion has A_2 symmetry, while the HOMO of cyanomethyl anion has B_2 symmetry. Since the A_2 irreducible representation transforms as a d_{xy} atomic function, the allyl anion should show a $E^{3/2}$ or smoothly rising p-wave energy dependence at threshold.[9] The B_2 representation transforms as a p_y atomic function; thus the cyanomethyl anion should show a $E^{1/2}$ or discontinuous s-wave energy dependence at threshold.

The experimental threshold behavior of these anions is contrasted and shown to be in good qualitative agreement with the expected behavior based on both group theory and a more quantitative formulation of the threshold law.[8] We then fit the experimentally measured cross sections to the calculated cross sections in the threshold region. From this treatment we obtain the electron affinities of the allyl and cyanomethyl radicals.

Experimental Section

Both the allyl and cyanomethyl anions were generated and trapped in a modified Varian V-5900 ion cyclotron resonance spectrometer.[10] The allyl anion was generated from propene via proton abstraction by OH^-. The OH^- was formed by dissociative electron capture by H_2O at 5.5 eV. Total pressure was 1×10^{-6} to 4×10^{-6} Torr consisting of approximately equal amounts of water and propene. Cyanomethyl anion was generated from acetonitrile via proton abstraction by F^-. The F^- was formed by dissociative electron capture by NF_3 at 1.7 eV. Total pressure in this case was about 5×10^{-7} Torr and consisted of about 80% acetonitrile and 20% NF_3. At these pressures the ions could be trapped for about 0.5 s.

The light source for the photodetachment experiments was a 1000 W xenon arc lamp used in conjunction with a grating monochromator.[11] A grating blazed at 1500 nm was used to collect data above 1000 nm for allyl anion with a resolution (fwhm) of 39.6 nm. All other data were obtained using a grating blazed at 600 nm and have a resolution
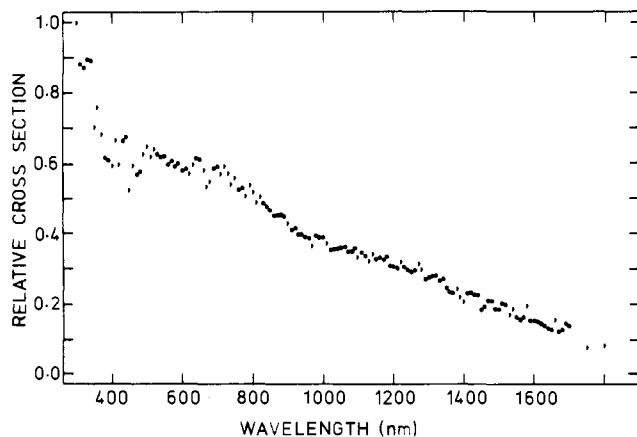
Figure 1. Relative photodetachment cross section for allyl anion. Resolution is 23.8 nm (fwhm) below 1000 nm and 39.6 nm (fwhm) above 1000 nm.

Figure 2. Relative experimental (●) and theoretical (—) photodetachment cross sections for cyanomethyl anion. Resolution for both experiment and theory is 23.8 nm (fwhm).

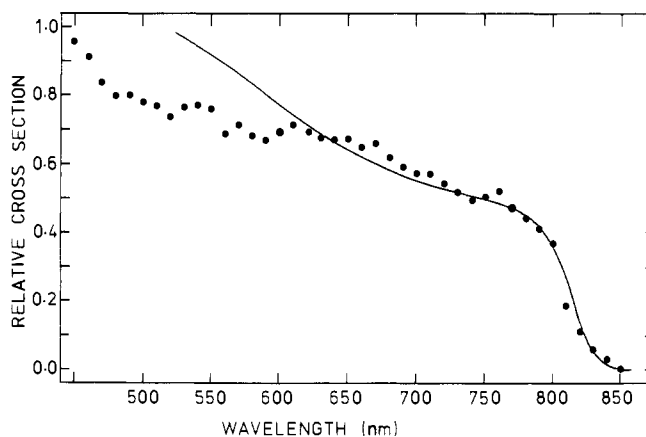(fwhm) of 23.8 nm. The collection and analysis of the data have been previously described.[10]

Results and Discussion

Threshold Shapes. At an electron energy of 5.5 eV O^-, OH^-, and H^- may be formed by electron impact on H_2O. Since all of these ions will abstract a proton from propene to form allyl anion, photodetachment of any of them will result in a decrease in the allyl ion signal. Therefore the photodetachment cross sections of O^-, H^-, and OH^- could be superimposed on the apparent cross section of allyl anion. The OH^- photodetachment amounted to about 35% of the total change in allyl ion signal, but since OH^- has a sharp threshold near 680 nm,[4] its contribution was easily subtracted from the total cross section. O^- has a sharp threshold near 850 nm, but since little evidence of a sharp transition around 850 nm is experimentally observed, no correction for O^- detachment has been made. The H^- photodetachment cross section has a slowly rising threshold which has an onset at 1750 nm, peaks at about 750 nm, and drops sharply below 600 nm. Since the experimental cross section for allyl anion after removal of the OH^- contribution showed none of these features, we conclude that the remaining cross section is predominantly due to photodetachment of allyl anion. The data are presented in Figure 1 with no correction for H^- detachment. The cross section for photodetachment of cyanomethyl anion is presented in Figure 2. Here there was no interfering detachment, since F^- has a threshold[12] at about 350 nm.

The data for allyl anion show a cross section which increases gradually with photon energy until just below 400 nm where a sharp increase in the cross section is observed. Both photon flux and cross section had become too low to observe photodetachment beyond 1850 nm. Cyanomethyl anion shows a sharp threshold at about 840 nm followed by a gradual rise in cross section with increasing photon energy.

For both ions the threshold areas must correspond to transitions from the ground electronic state of the anion to the ground electronic state of the radical. In both cases the photon energies near threshold are probably too low to reach an excited state of the anion.[13] It is quite possible however that the sudden increase in cross section for allyl anion below 400 nm is due to an electronic transition in the anion followed by autodetachment.[14]

We expect the initial vibrational state of these ions to be primarily the ground state since if the ions were formed in an initially hot vibrational state, at these pressures it seems reasonable to assume they would be essentially thermalized well within 500 ms.[15] Thus nonthermal hot bands should be no greater than about 50% of the intensity of the transition originating at the ground state. We expect the hot bands to be weak here because the populations in excited vibrational states are low and because of small off-diagonal Franck-Condon factors. In addition, the proton abstraction reactions by which both allyl and cyanomethyl anions are formed will be shown to be only slightly exothermic, making it unlikely that large numbers of ions are produced in highly excited vibrational states. For cyanomethyl anion only one sharp transition is observed over about 30 nm, with no measurable vibrational hot bands at longer wavelengths.

The electron affinities discussed in the next section may be used with known bond strengths to determine the exothermicity of the reactions by which the allyl and cyanomethyl ions are formed. Using 12.7 ± 1.2 kcal/mol for $EA(CH_2=CH—CH_2\cdot)$, $\Delta S° = 0.8$ eu,[16] $DH°(CH_2=CHCH_2—H) = 89 \pm 2$ kcal/mol,[17] $DH°(HO-H) = 119$ kcal/mol,[18] and $EA(OH\cdot) = 42.2$ kcal/mol[4] for the reaction

$$OH^- + CH_2=CH—CH_3 \rightarrow CH_2=CH—CH_2^- + H_2O$$
(2)
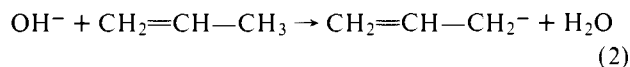
$\Delta G°$ is determined to be -0.7 ± 3.1 kcal/mol. Similarly, using $EA(CH_2CN) = 34.8 \pm 0.4$ kcal/mol, $DH°(H-F) = 135.8$ kcal/mol,[19] $EA(F\cdot) = 78.5$ kcal/mol,[20] $DH°(H-CH_2CN) = 92.9 \pm 2.5$ kcal/mol,[21] and $\Delta S° = 4.4$ eu[22] for the proton abstraction from acetonitrile by F^-, this proton abstraction is found to have $\Delta G° = -0.5 \pm 2.9$ kcal/mol. Thus both of these reactions are only slightly exothermic, as was pointed out in discussing the possibility of the ions being formed vibrationally hot.

Vibronic transitions from the ground state of each ion are allowed to a number of vibrational levels of the radical. The intensities of the various transitions depend on the differences in geometry between the anion and radical. In the case of both allyl and cyanomethyl anions, the HOMO (from which the electron is being detached) is essentially a nonbonding orbital. Loss of an electron from this nonbonding orbital should not change the geometry of the system substantially as only the nonbonding interactions will be affected. Therefore we expect the geometries of the anion and radical to be quite similar in both cases. To test this expectation we have done geometry optimization calculations[23] (using CNDO and INDO approximations) for the cyanomethyl anion and radical. Both CNDO and INDO give substantially the same results, very little geometry change in going from anion to radical. All bond lengths showed less than 0.008 Å change and all angles less than 1.8° change. Based on these calculations, better than 99% of the transition intensity should involve no change in vibrational state.[24] Again, due to the nonbonding nature of the

HOMO, allyl anion is similarly expected to show only diagonal vibronic transitions.

The cross section is therefore expected to be composed of a superposition of all possible rotational transitions between the vibrational ground states of the anion and radical. The allyl and cyanomethyl systems[25] may be closely approximated as prolate symmetric tops,[26] in which case (neglecting spin-rotation splitting) the intensities of the rotational transitions are given by the Hönl-London formulas.[27]

At this point, we calculate the cross section for a single rotational transition using a partially orthogonalized plane-wave final state and the CNDO/2 coefficients[23] of the HOMO for the initial state of the electron to be detached.[8] These HOMO's are $\psi_{allyl} = 0.7071\phi_{py}(C_1) - 0.7071\phi_{py}(C_3)$ and $\psi_{cyanomethyl} = 0.7617\phi_{py}(C_1) + 0.0327\phi_{py}(C_2) - 0.6471\phi_{py}(N)$. We then sum this cross section over all possible rotational transitions, weighting each one by its relative intensity. The resultant cross section when convoluted with the instrumental bandwidth should be directly comparable (outside an overall normalization) to the experimental cross sections near threshold. These curves are shown in Figures 1 and 3 with the experimental data in the threshold region.

The theoretical curves have been fitted to experiment only within 1 eV of threshold. Because of symmetry, the theoretical curves must be essentially correct right at threshold. But above threshold, only qualitative agreement should be expected. The calculated curves quantitatively serve only as a rough guide then in extracting the photodetachment thresholds.

The agreement of the calculated cross sections with the experimental data near threshold is very good considering the theoretical model which we have used for photodetachment. Large discrepancies between calculated and experimental cross sections do not begin to appear until about 1 eV above threshold in both cases. This agreement indicates the cross section for photodetachment may be accurately described near threshold by time-dependent perturbation theory (in a 1 electron approximation) in which the initial state of the electron is a molecular orbital and the final state is a plane wave orthogonalized to the original orbital. We expect the plane wave to be a reasonable description of the detached electron for low photoelectron energies since the interactions between the radical and the detached electron are primarily short ranged polarization potentials. The agreement with experiment confirms this expectation. The orbitals describing the initial state of the electron are the highest occupied molecular orbitals from CNDO/2 calculations. The radial diffuseness of these orbitals was increased, as described in ref 8, by decreasing the normal Slater exponents to the values 0.56 for carbon and 0.40 for nitrogen. The cross section for cyanomethyl anion is quite sensitive to the form of the orbital; the HOMO coefficients must be within about 10% of the values given by CNDO to obtain a cross section resembling the experimental data. Noting the agreement obtained, we conclude that the CNDO description of the HOMO of this anion is quite good, if it is recognized that the orbital is actually much more diffuse than molecular orbitals are in neutral compounds.[28]

Electron Affinities. The electron affinities of the allyl and cyanomethyl radicals may now be obtained. We define the electron affinity as the energy difference between the lowest rotational-vibrational state of the anion and the lowest rotational-vibrational state of the radical (0,0 → 0,0 transition). For cyanomethyl anion the onset for the 0,0 → 0,0 transition determined by fitting the theoretical to the measured cross section is 823 ± 10 nm. The error limits are made broader than the ±4 nm from the monochromator calibration uncertainty, so as to reflect possible errors in the fitting procedure resulting from noise in the data points.

For allyl, the lack of data out to threshold makes it difficult to obtain an accurate electron affinity. However, we may ob-
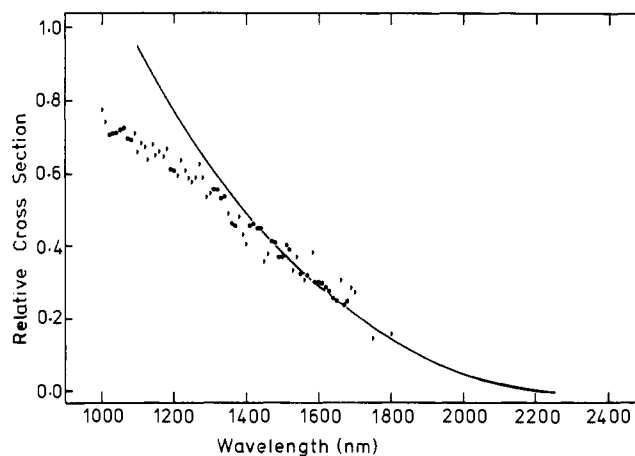
Figure 3. Relative experimental (●) and theoretical (—) photodetachment cross sections for allyl anion near threshold. The experimental data are the same as in Figure 1; the theoretical cross section has not been convoluted with an instrumental slit function.

tain an upper limit from the reaction

$$CH_3O^- + CH_2{=}CH{-}CH_3 \rightarrow CH_2{=}CH{-}CH_2^- + CH_3OH \quad (3)$$
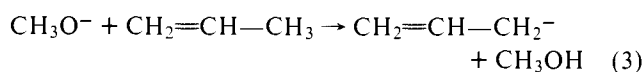
which does not occur (ΔH° positive). Using DH°(CH$_3$O-H) − EA(CH$_3$O·) = 64.5 kcal/mol[29] and DH°(CH$_2$=CHCH$_2$—H) = 89 ± 2 kcal/mol[17] and neglecting entropy changes we obtain an upper limit on EA-(CH$_2$=CH—CH$_2$·) of 24.5 kcal/mol. But reaction 2 may be used to obtain a lower limit; ΔG° is negative since this reaction occurs readily. Using the previously defined DH°(H$_2$O) and EA(OH·) and neglecting entropy changes we obtain a lower limit on EA(CH$_2$=CH—CH$_2$·) of 12.2 kcal/mol. Therefore 12.2 ≤ EA(CH$_2$=CH—CH$_2$·) ≤ 24.5 kcal/mol which corresponds to a threshold lying between 1170 and 2345 nm. A linear extrapolation of the data in Figure 3 to threshold gives about 2020 nm. Since theory predicts the cross section to approach threshold with a decreasing slope, the actual threshold is expected to lie to wavelengths longer than 2020 nm. Within these limits we fit the theoretical curve to the experimental data (see Figure 3) and obtain a threshold of 2254 ± 200 nm. The error limits here result entirely from the fitting procedure and were chosen so as to extend from just above the wavelength obtained from a linear extrapolation of the data to well beyond the upper wavelength limit imposed by reaction 2.

Thus we have identified the following electron affinities:

EA(CH$_2$CN·) = 1.507 ± 0.018 eV

(34.8 ± 0.4 kcal/mol)

EA(CH$_2$=CH—CH$_2$·) = 0.550 ± 0.054 eV

(12.7 ± 1.2 kcal/mol)

This value for the electron affinity of cyanomethyl radical is in reasonable agreement with a previous estimate of ≥1.6 eV made from electron impact threshold measurements.[30] It is somewhat lower than the 40.3 ± 2.9 kcal/mol inferred from the gas-phase acidity measurements of McMahon and Kebarle[31] and the H–CH$_2$CN bond strength.[21]

Our electron affinities may be combined with the known H–CH$_2$CN and CH$_2$=CHCH$_2$—H bond strengths of 92.9 ± 2.5 and 89 ± 2 kcal/mol respectively to calculate the absolute acidities of acetonitrile and propene. These absolute acidities are 371.8 ± 2.9 and 389.9 ± 3.0 kcal/mol for acetonitrile and propene, respectively. We note that this value for acetonitrile is 5.5 kcal/mol higher than that of McMahon and Kebarle.[31,34]

One very interesting aspect of the electron affinity of the allyl radical is the comparison of the resonance energy in the radical and anion. The resonance energy of the allyl radical is given as 9.6 ± 1.5 kcal/mol by Golden, Rodgers, and Benson[32] and is only slightly less than its electron affinity. If the electron affinity of the undelocalized vinyl methyl radical $CH_2=CH—CH_2\cdot$ is known, the resonance energy, RE, of the allyl anion may be calculated. It is given by

$$RE(CH_2=CH=CH_2^-) = RE(CH_2=CH=CH_2\cdot)$$
$$+ EA(CH_2=CH=CH_2\cdot) - EA(CH_2=CH—CH_2\cdot)$$

We estimate the electron affinity of the undelocalized vinyl methyl radical, $CH_2=CH—CH_2\cdot$, as ≤ 7.8 kcal/mol.[33] This gives the resonance stabilization of the allyl anion as $\gtrsim 14.5$ kcal/mol.

This is greater than the resonance energy of the allyl radical, a result which might be expected since electron repulsion will be more important in the anion and delocalization should play an important role in promoting correlation.

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References and Notes

(1) S. J. Smith and D. S. Burch, Phys. Rev., **116**, 1125 (1959).
(2) L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, Phys. Rev., **111**, 504 (1958).
(3) W. C. Lineberger and B. J. Woodward, Phys. Rev. Lett., **25**, 424 (1970).
(4) H. Hotop, T. A. Patterson, and W. C. Lineberger, J. Chem. Phys., **60**, 1806 (1974).
(5) J. H. Richardson, L. M. Stephenson, and J. I. Brauman, Chem. Phys. Lett., **25**, 318 (1974).
(6) E. Herbst, T. A. Patterson, and W. C. Lineberger, J. Chem. Phys., **61**, 1300 (1974).
(7) K. C. Smyth and J. I. Brauman, J. Chem. Phys., **56**, 5993 (1972).
(8) K. J. Reed, A. H. Zimmerman, H. C. Andersen, and J. I. Brauman, J. Chem. Phys., **64**, 1368 (1976).
(9) The cross section at threshold is proportional to $E^{\ell+1/2}$ where ℓ is the "angular momentum" of the photoelectron. The dipole selection rule gives $\Delta\ell = \pm 1$.
(10) K. C. Smyth and J. I. Brauman, J. Chem. Phys., **56**, 1132 (1972).
(11) K. J. Reed and J. I. Brauman, J. Chem. Phys., **61**, 4830 (1974).
(12) A. Mandl, Phys. Rev. A, **3**, 251 (1971).
(13) For acetonitrile and propene electronic transitions occur at wavelengths lower than 300 nm. Although some shift to the red is expected in the anions due to the more extensive delocalization it seems unlikely that a shift of 2.5 eV could occur to shift these transitions out to 800 nm.
(14) J. H. Richardson, L. M. Stephenson, and J. I. Brauman, J. Chem. Phys., **62**, 1580 (1975).
(15) V–V energy transfer is efficient, occurring in less than 100 collisions in large organic molecules. See J. D. Lambert and R. S. Rowlinson, Proc. R. Soc. London, Ser. A, **204**, 424 (1950).
(16) This entropy change is $R \ln \frac{3}{2}$ arising from propene having three equivalent allylic protons and water having two protons.
(17) D. M. Golden and S. W. Benson, Chem. Rev., **69**, 125 (1969).
(18) J. A. Kerr, Chem. Rev., **66**, 465 (1966).
(19) S. W. Benson, J. Chem. Educ., **42**, 502 (1965).
(20) R. S. Berry and R. Milstein, J. Chem. Phys., **55**, 4146 (1971).
(21) K. D. King and R. D. Goddard, Int. J. Chem. Kinet., **7**, 837 (1975).
(22) Obtained from the standard entropies of the neutrals and the entropies of the neutrals isoelectronic to the anions. Values from S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.
(23) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970; P. A. Dobosh, CNINDO, Program 141, Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind. 47401.
(24) This number was calculated assuming uncoupled harmonic oscillators and no vibrational frequency difference between anion and radical.
(25) The final state is considered to be a radical–electron complex in considering rotational transitions.
(26) The asymmetry parameters are -7.23×10^{-5} and -2.35×10^{-2} for cyanomethyl and allyl anions, respectively (see ref 27, p 105).
(27) G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand-Reinhold, New York, N.Y., 1966, p 226.
(28) The diffuse nature of these orbitals is reflected in the first "ionization potentials" which are on the order of 1 eV for these anions. For most neutrals this ionization potential is about 8 eV, indicating a much more tightly bound electron.
(29) R. T. McIver, Jr., and J. S. Miller, J. Am. Chem. Soc., **96**, 4323 (1974), and personal communication.
(30) S. Tsuda, A. Yokohata, and T. Umaba, Bull. Chem. Soc. Jpn., **44**, 1486 (1971).
(31) T. B. McMahon and P. Kebarle, J. Am. Chem. Soc., **98**, 3399 (1976).
(32) D. M. Golden, A. S. Rodgers, and S. W. Benson, J. Am. Chem. Soc., **91**, 2136 (1969).
(33) Since NH_2^- fails to abstract a proton from ethane [$DH°(NH_3) = 107.4$ kcal/mol (D. K. Bohme, R. S. Hemsworth, and H. W. Rundle, J. Chem. Phys., **59**, 77 (1973)) and $DH°(CH_3CH_2-H) = 98$ kcal/mol ("CRC Handbook of Chemistry and Physics", 52nd ed, 1971); $EA(NH_2\cdot) = 17.2$ kcal/mol (K. C. Smyth and J. I. Brauman, J. Chem. Phys., **56**, 4620 (1971)] this abstraction should be an endothermic reaction, implying $EA(CH_3CH_2\cdot) \leq 7.8$ kcal/mol. We have neglected the stabilizing effects of a vinyl group in using this as the $EA(CH_2=CH—CH_2\cdot)$.
(34) NOTE ADDED IN PROOF. Recent work by P. Kebarle (Alberta) resolves the discrepancy between the acidity of acetonitrile reported in Ref. 31 and that inferred in this work (P. Kebarle, personal communication).

Application of Photoelectron Spectroscopy to Intramolecular Hydrogen Bonding. 5. The X-Ray Photoelectron Spectra of cis- and trans-2-Substituted Cyclanols

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Abstract: The technique of x-ray photoelectron spectroscopy has been used to determine the binding energy shifts in the 1s orbitals of the heavy atom termini of an intramolecular H bond relative to those in a geometric isomer whose structure precludes H-bond formation. When E_B shifts could be detected, the electron donor atom becomes harder to ionize and the electron acceptor atom easier to ionize on H-bond formation. Such shifts cannot simply be a consequence of changing geometric isomers, since these changes produce no such shifts in the absence of H bonding. The direction of the shifts is qualitatively predicted by existing ab initio calculations on related systems, although such calculations do not take account of excited-state electron distributions. A CNDO/2 potential model based charge shifts within the molecule fails to account for the observed results.

Recently the phenomenon of H bonding has been studied by several sophisticated computational techniques.[1-7] Except for extended Hückel methods[2a] (EHT), calculations on H-bonded systems using semiempirical[2] and ab initio methods[3-7] agree on the general charge redistributions occurring on H-bond formation. For example, in 1,3-propanediol[3b] (**1**), the