imental points of Figure 8, and then applying a propagation of errors treatment. In this analysis, the extinction coefficients were considered to be constant since arbitrary variations of a few percent result in physically unrealistic concentrations (large negative values and/or sums which substantially exceed the initial ground-state concentration).

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(44) After this manuscript was completed, a paper appeared (R. Bensasson, E. A. Dawe, D. A. Long, and E. J. Land, *J. Chem. Soc.*, *Faraday Trans. 1*, **73**, 1319 (1977)) which reports $\epsilon^{445}_{\mathrm{AT\text{-}T}} = 1.14 \times 10^5\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ (±15%) in *n*-hexane. While we are unable to account for the large discrepancy between this value, which was determined by a pulse radiolysis–energy transfer technique, and ours of $7.0 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ (±10%), we may note that the higher value is inconsistent with the saturation of triplet state absorption at relatively low laser pulse energies (Figure 2).

Detection and Investigation of Allyl and Benzyl Radicals by Photoelectron Spectroscopy

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Abstract: Allyl and benzyl radicals have been produced by pyrolysis in a photoelectron spectrometer. Adiabatic and vertical IPs coincide for both species and are determined to be 8.13 ± 0.02 eV for allyl, 7.20 ± 0.02 eV for benzyl, and 7.22 ± 0.02 eV for benzyl-α-d_2. Heats of formation derived from these results are 225.5 ± 1.1 kcal/mol for allyl cation and 211 ± 1.1 kcal/mol for benzyl cation. Vibrational structure has been resolved. The results are discussed in terms of the role of the unpaired electron in the conjugated π systems of these radicals.

Application of various spectroscopic techniques to free radicals has provided a great deal of information on their electronic structure, geometries, spin densities, and normal modes. Recently, photoelectron spectroscopy (PES) has been added to the list of techniques available, allowing characterization of the relationship between the radical and its ion. In particular, the first photoelectron band yields information on the unpaired electron in the radical. Much can be learned about the localization and bonding character of this electron by consideration of the shape of the band itself, especially when vibrational structure is present. The information obtained can be combined with that from other sources such as electron spin resonance spectroscopy (ESR) and theoretical calculations to characterize stabilities and reactivities of these transient species. Radicals having conjugated π systems are particularly well studied. Allyl and benzyl radicals are among the simplest and best understood of these, and are the subject of the present work.

Both of these species have been treated in numerous theoretical calculations.[1] Many of these involve interpretation of ESR hyperfine splittings[2-5] in terms of spin densities, which give information on the delocalization of the unpaired electron. In allyl radical,[2,3] the positive density is found entirely on the equivalent terminal carbon atoms, with a small negative component on the central carbon. In benzyl radical,[4,5] on the other hand, the spin density on the exo methylene is $\sim$0.7–0.8, the remainder being shared between the ortho and para positions on the phenyl ring. The distribution of unpaired spin in these two radicals can be understood qualitatively in terms of valence bond resonance structures.

Theoretical effort has also been directed toward an understanding of the electronic structure of allyl[6-9] and benzyl[10-13] radicals. Analyses of the absorption and emission spectra of benzyl radical have identified the symmetries of the states involved, as well as most of the normal modes in the ground state.[10-13] However, owing to the large number of electrons in benzyl radical, only allyl radical has been the subject of ab initio calculations involving large basis sets.[6-9]

Both molecular orbital[6-8] and generalized valence bond (GVB)[7-9] calculations indicate that the unpaired electron in allyl radical is mainly nonbonding. Levin and Goddard[7,8] found that this species is reasonably well described using wave functions of an ethylene molecule fused to methylene. Removal of this electron to form a carbonium ion allows the two remaining π electrons to delocalize over all three centers.[14] This increased delocalization is expected to increase the resonance energy of the ion relative to that of the neutral.[15]

The results of the present work are consistent with the spin density distributions derived from ESR studies. They also support the theoretical description of allyl radical discussed above, and indicate that a similar one is appropriate for benzyl radical.

Experimental Section

These experiments are part of a series of studies of free radicals produced by pyrolysis of alkyl nitrites. The instrumentation, which has been briefly described in a previous communication,[16] consists of a photoelectron spectrometer of standard design which has been specifically modified to study the products of gas-phase pyrolyses. A schematic of the spectrometer is shown in Figure 1. The differentially pumped source chamber, 127° electrostatic analyzer, and Channeltron electron multiplier are situated on a stainless steel baseplate in a high-vacuum chamber. The HeI capillary discharge lamp, located directly underneath the source chamber, is separated from the main vacuum chamber by a stage of differential pumping. The analyzer is protected from magnetic fields by a mumetal shield and a set of six Helmholtz coils. Sample gases are introduced into the source chamber through a stainless steel inlet system divided into three sections. Two of these are connected to the bottom of the source chamber and are used for calibrant gases (usually argon) and samples at room temperature. The third enters the vacuum chamber through the side wall. It consists of a 3-mm i.d. quartz tube fitted to a stainless steel flange. This tube is used for pyrolysis. A 2-cm long section at the free end of the tube is wrapped with double-stranded Semflex heater wire insulated with MgO and an Inconel outer sheath. A chromel-constantan thermocouple is wedged between the sheath and the quartz tube to monitor the temperature. Constant temperatures of up to 1000 °C can be maintained for hours. The analyzer is protected from blackbody radiation by a water-cooled copper shield surrounding the hot section. The tip of the quartz tube is inserted through an aperture in the side

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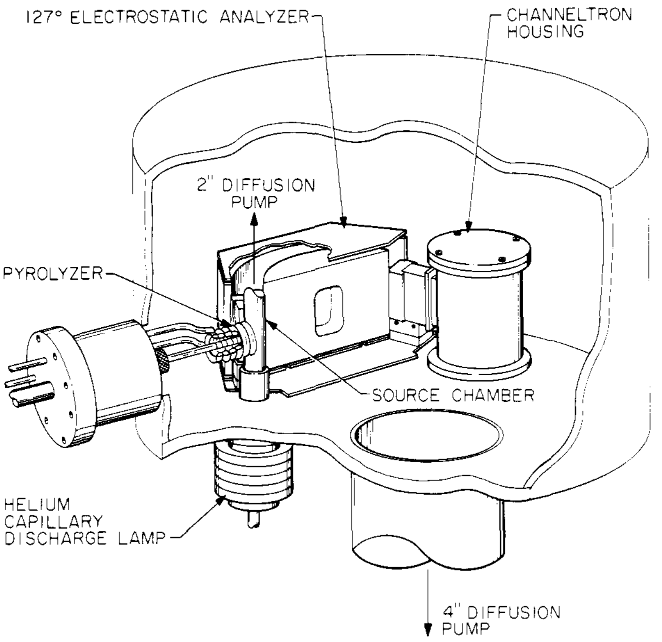

Figure 1. Schematic of photoelectron spectrometer used in these experiments.

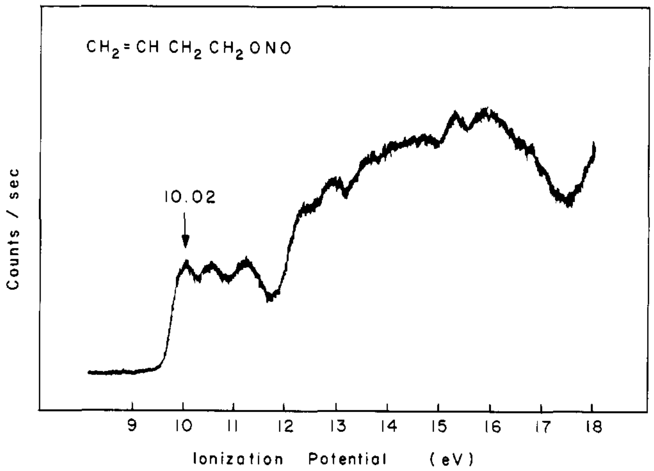

Figure 2. Photoelectron spectrum of 3-butenyl nitrite.

of the source chamber, such that the hot gases traverse a 0.75-cm path before intersecting the photon beam at a 90° angle. Electrons ejected normal to this plane are energy analyzed.

Allyl and benzyl radicals were produced by the pyrolysis of 3-butenyl nitrite and 2-phenylethyl nitrite.[17]

$$CH_2{=}CHCH_2CH_2ONO \rightarrow CH_2{=}CHCH_2CH_2O\cdot + NO \quad (1)$$

$$\hookrightarrow CH_2{=}CHCH_2\cdot + CH_2O$$

$$C_6H_5CH_2CH_2ONO \rightarrow C_6H_5CH_2CH_2O\cdot + NO \quad (2)$$

$$\hookrightarrow C_6H_5CH_2\cdot + CH_2O$$

The nitrites were prepared from 3-buten-1-ol and 2-phenylethanol (Aldrich) using standard procedures.[18] The 2-phenylethanol-d_2 used to make benzyl-α-d_2 radicals was prepared by solvolysis, deuteration, and reduction of a sodium salt of diethyl phenylmalonate.[19] The extent of deuterium incorporation was checked by NMR, and found to be > 97 ± 5%. The isotopic purity obtained was quite adequate for PES, which has a rather low sensitivity to compounds present in small quantities.

All spectra were recorded using a Tracor-Northern NS570A multichannel scalar with a 4K memory. The quartz tube used for pyrolysis was heated to ~730 °C for these experiments, although the effective temperature of the gases was somewhat lower owing to low pressures and short contact times. Decomposition of the nitrites was complete. Room temperature spectra were calibrated with argon. The free-radical spectra were calibrated using the first bands of NO and CH_2O, produced in the pyrolysis of the nitrites. Resolution was moderate, averaging between 30 and 40 meV fwhm as determined from the Ar peaks. The IPs reported here are the average of several determinations, and a reasonable estimate of the error is ±0.02 eV. The vibrational spacings observed were reproducible to within ±0.005 eV. Typical radical count rates were 20 and 60 s^{-1} for benzyl and allyl, respectively.

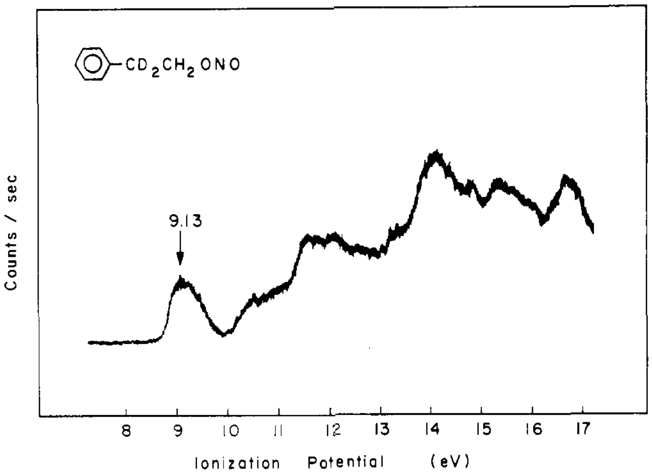

Figure 3. Photoelectron spectrum of 2-phenylethyl nitrite-d_2.

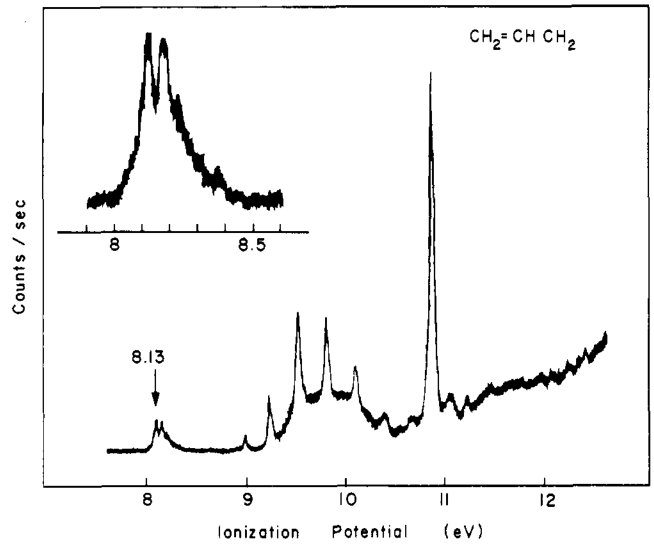

Figure 4. Pyrolysis spectrum of 3-butenyl nitrite containing the first band of allyl radical. NO and CH_2O are at 9-10 and 10.88 eV, respectively. The small peak at 9.0 eV is the HeIβ ionization of CH_2O.

Results

The spectra of the parent nitrites are shown in Figures 2 and 3. The spectrum of 2-phenylethyl nitrite, which is not included, is identical with that of the deuterated species, and also has a vertical first IP of 9.13 eV. The first bands of the allyl, benzyl, and benzyl-α-d_2 radicals are presented in Figures 4 and 5.

Taking the vertical ionization potential to be the point of maximum intensity of a photoelectron band, it can be seen in Figures 4 and 5 that the vertical and adiabatic ionization potentials of each of the two radicals coincide. The IPs are determined to be 8.13 eV for allyl, 7.20 eV for benzyl, and 7.22 eV for benzyl-α-d_2. The features observed at lower ionization energy than the band maxima in Figures 4 and 5 are attributed to hot bands, as their intensity relative to that of the main bands varied strongly with temperature and pressure. A single strong vibrational progression is resolved in each peak, although other

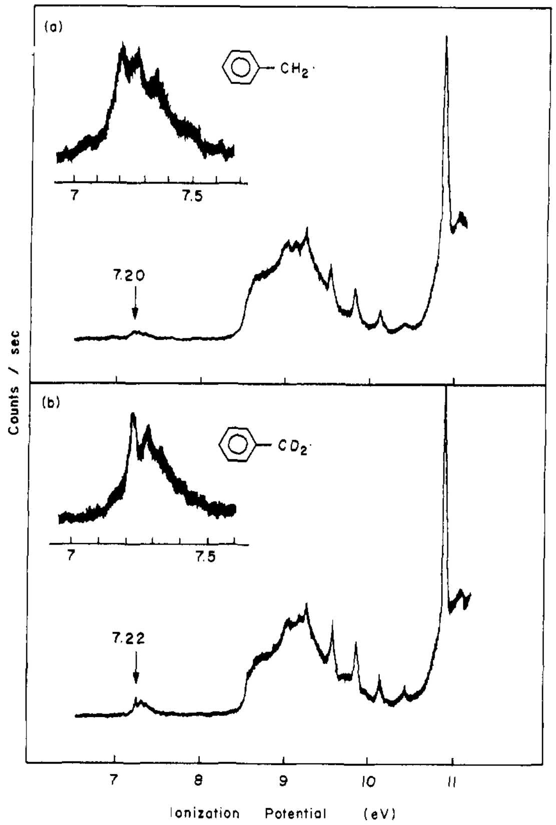

Figure 5. Pyrolysis spectra of 2-phenylethyl nitrite. NO and CH_2O are at 9–10 and 10.88 eV, respectively. The small peak at 9.0 eV is the HeIβ ionization of CH_2O: *(a) the first band of benzyl radical; (b) the first band* of benzyl-α-d_2 radical.

modes are undoubtedly excited as evidenced by the poor resolution of the higher vibrational states of the ion. The spacing in allyl is 0.05 eV or 420 cm^{-1}. An isotope effect is observed on α-deuterium substitution in benzyl. The observed frequency shifts from 0.07 (560 cm^{-1}) to 0.06 eV (480 cm^{-1}). Assignment of these vibrations will be discussed below.

The primary pyrolysis products of the alkyl nitrites are an alkyl radical, CH_2O, and NO, as shown in eq 1 and 2. The bands of these species are clearly present in Figures 4 and 5. The spectra also have a rather broad band at ~9–10 eV, underlying the NO peaks. Determination of the origin of this band requires knowledge of the chemistry of the radical as well as alternate decomposition pathways of the precursor. Even with this information, definitive assignments are difficult at best.

Alkyl nitrites have been shown to decompose by a secondary pathway,[17] forming an aldehyde and HNO. In the case of 2-phenylethyl nitrite, the aldehyde formed is phenylacetaldehyde. Although the first PE band of this species starts at about 8.6 eV,[20] the spectrum has a second band between 10 and 11 eV which is not present in the pyrolysis spectra. The aldehyde is thus not a major product under our conditions. Hydrogen abstraction by benzyl from organic deposits on the furnace walls will form toluene. PE bands from toluene[21] can be identified in the full pyrolysis spectrum, and thus will also contribute to the complex band at 9 eV. Using this information, the toluene and NO bands can be subtracted out, as shown in Figure 6, leaving three more smooth bands. The bands at ~8.8 and 9 eV do not correspond to any obvious reaction products, and remain unassigned.

The first excited state of benzyl cation, $^3B_1$, has been calculated to lie 2.30[22] and 2.45 eV[23] above the ground state. Combination of these values with the first IP of benzyl radical leads to a prediction of 9.50 and 9.65 eV for the second IP. These energies are typical of ionizations involving the ring π systems of monosubstituted benzenes. The component of the complex band that is centered at 9.6 eV has been observed to be proportional in height to the first benzyl radical band in these experiments. On the basis of the above evidence, this component is tentatively assigned to the $^3B_1$ state of the ion.[24] Excitation to this state from the ground state of the ion by ultraviolet absorption spectroscopy is spin forbidden, and thus has not been observed. The absorption spectrum of benzyl cation is not very well known. One study[25] showed that substituted benzyl cations typically absorb in the 300- (4 eV) and 400-nm (3 eV) region. Recently, a band assigned to the benzyl cation has been observed at 363 nm (3.42 eV).[26] No prominent unassigned bands are found at 10.2 or 10.6 eV in the photoelectron spectrum.

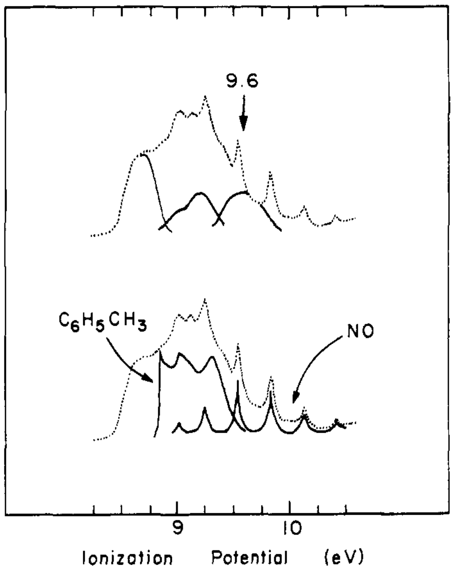

Figure 6. Sketch of the second band found in Figures 4a and 4b. The components which are identified are toluene and NO. The band centered at 9.6 eV is tenatively assigned to the $^3B_1$ state of benzyl cation.

The situation is not as clear for 3-butenyl nitrite. The PE spectrum and IP of 3-butenal are unknown, although by analogy with other small aldehydes the first band can be expected to be between 9.5 and 10 eV.[27] However, the ionization of these aldehydes typically involves a nonbonding electron, and the band would not be expected to be as broad as is observed. The first excited state of allyl cation, $^3B_2$, has been calculated to be 3.01[14] and 3.67 eV[6] above the ground state, and hence is not likely to give rise to the observed band. (A discrete band at 11.1 or 11.8 eV could not be identified.) Propylene, which can be formed by hydrogen abstraction, has a characteristic sharp band at 9.9 eV[28] that is absent from the spectrum. Assignment of this band (and the remaining bands in the benzyl spectrum) requires further information concerning the chemistry of the nitrites under low-pressure, fast-flow conditions.

Discussion

The results of the present experiments have provided information which can be used to examine the thermochemistry of benzyl and allyl radicals and their ions. The observed vibrational progressions can be discussed in terms of the relationship between the neutral and ionic structures of both species.

Thermochemistry. The thermochemistry of allyl and benzyl cations has been the subject of some disagreement in the literature of the past 20 years because of uncertainties in the ionization potentials of the radicals, and in the interpretation of appearance potentials of fragment ions. Theoretical ionization potentials[6,8,29] and heats of formation[30] obtained from both semiempirical and ab initio calculations disagree with each other and with experiment, including the results of the present work. The allyl radical IP reported here is 8.13 eV, in closer agreement with the higher of the two values of 8.07 ± 0.03[31] and 8.16 ± 0.03 eV[32] determined by Lossing. In general, electron impact ionization potentials are upper limits to the adiabatic values. Extension of the onset of the ionization efficiency curve below 8.13 eV in ref 31 may possibly be due to hot bands, which are thought to be present in our spectra.

The heat of formation of allyl cation calculated using IP (allyl radical) = 8.13 eV and ΔH_f (allyl radical) = 38 kcal/mol[33] is 225.5 ± 1.1 kcal/mol. Previous determinations of this number have ranged from 214 to 232 kcal/mol.[34] The most recent and consistent determinations have been 226 ± 2,[35] 224.5 ± 1,[34] and 227 kcal/mol.[36] The present value can be seen to be in excellent agreement with these data, confirming the currently accepted heat of formation of allyl cation. If a value of 40.6 kcal/mol[37] is used for heat of formation of allyl radical, the ionic heat of formation becomes 228.1 kcal/mol, which is too high.

The IP of benzyl radical determined in this work is 7.20 eV. An earlier photoelectron spectroscopic study gave 7.43 ± 0.06 eV for the vertical IP.[38] The present value is in good agreement with an electron impact determination of $\leq$7.27 ± 0.03 eV,[31] but substantially lower than earlier determinations of 7.73 ± 0.08[32] (electron impact) and 7.63 eV[39] (photoionization). Lossing[31] reconciled his two measurements by noting that the curvature of the onset of the ionization efficiency curve had been underestimated in the earlier work. The discrepancy between the electron and photon impact values remained, and it was suggested that the electron impact ionization could occur via an autoionization process forming cycloheptatrienyl cation, then thought to be much more stable than benzyl cation. This process might be forbidden in photoionization. The present experiments eliminate the necessity for a dual ionization mechanism in benzyl, and confirm Lossing's electron impact result.

The heat of formation of benzyl cation is calculated to be 211 ± 1.1 kcal/mol, using a value of 45 ± 1 kcal/mol[33] for the heat of formation of the radical. This agrees with the value determined by Lossing,[31] 213 kcal/mol. The present work confirms emerging evidence that the cycloheptatrienyl and benzyl cations have nearly equal heats of formation. Using 209 kcal/mol[40] for the heat of formation of cycloheptatrienyl cation, the rearrangement of benzyl cation to the seven-membered ring is found to be exothermic by about 2 kcal/mol, in agreement with 2.5 ± 0.3 kcal/mol as determined by Dunbar in studies of the photodissociation of toluene ions.[41]

The present result can be used to reexamine a recent communication by Abboud, Hehre, and Taft[42] involving halide transfer studies in an ion cyclotron resonance spectrometer. They measured a ΔH for the equilibrium between benzyl chloride and the *tert*-butyl cation. Combining this value with currently accepted heats of formation, they obtained a ΔH_f (benzyl cation) of 217.2 kcal/mol. This number was confirmed by STO4-31G calculations. Both our results and those of Lossing yield a much lower value. This discrepancy can be resolved if the heat of formation of the *tert*-butyl cation is 4-8 kcal/mol *lower* than the current value of 169 kcal/mol. This possibility is supported by recent photoelectron spectroscopic studies of the *tert*-butyl radical.[43,44] They reveal that a substantial amount of geometrical change occurs on ionization, and therefore that the adiabatic IP is lower than the vertical IP. The vertical IP is the number upon which the value of 169 kcal/mol is based. Work is currently in progress in our laboratory to clarify this situation further.

Vibrational Progressions. The coincidence of the adiabatic and vertical ionization energies in allyl and benzyl radicals indicates that the ion geometry is essentially the same as that of the radical in each species. This implies that the ejected electron was largely nonbonding in the neutral. However, the photoelectron bands are not single sharp peaks: at least three members of a vibrational progression can be distinguished in each band, and the presence of other low-intensity progressions cannot be ruled out. Ejection of a purely nonbonding electron would not be expected to produce vibrationally excited ions. Therefore, a certain amount of bonding or antibonding character must also be present in both radicals. A choice between the two possibilities can be made as follows for the case of benzyl radical.

Comparison of the IPs of benzyl and benzyl-α-d_2 radicals reveals the presence of a 0.02-eV isotope effect. Consideration of the inequality relating the IPs reveals that the difference between the isotopic frequencies in the neutral is greater than in the ion. Therefore, the curvature of the ionic hypersurface in the region of this mode is lower than in the neutral, and it can be concluded that the ejected electron had a certain amount of bonding character.

In cases where symmetry is preserved, the selection rules for single quantum vibrational transitions in PES require that only totally symmetric modes may be excited. If a group of modes are excited, that group must contain a totally symmetric mode. Excitation of modes of other symmetry involves transitions of two quanta. Progressions resulting from two quantum transitions tend to lose intensity extremely rapidly owing to poor Franck-Condon overlaps.[45] An example of this can be found in the first photoelectron band of methyl radical.[46] The spectra shown in Figure 5 do not exhibit such a rapid drop in intensity. It is unlikely, therefore, that the observed progressions result from excitation of a single non-totally symmetric mode.

The frequency of the vibration in benzyl cation is rather low, and exhibits a modest isotope effect. The presence of a shift indicates that the mode involves the exo methylene group. Two possible assignments can be made. If it is assumed that the mode involved is totally symmetric, then it is most likely to be a symmetric deformation of the methylene group. The corresponding mode in benzyl radical, whose frequency would be an upper limit to that of the cation, has not been observed.[12] In ethylene,[21] the frequency of this deformation is 1342 cm^{-1}, and is not thought to decrease much in the ground state of the ion. The frequencies observed in these experiments are much lower, but the possible assignment cannot be ruled out. An alternative explanation is that several frequencies are excited at once, and that the progression involves excitation of the 1170-cm^{-1} vibration and a 585-cm^{-1} vibration. The higher energy mode would be totally symmetric, while the lower energy mode would have a different symmetry. A plausible assignment under this assumption is that both a phenyl-CH_2 stretch and torsion are excited. This is analogous to the first photoelectron band of ethylene,[21] which exhibits frequencies of 1230 and 430 cm^{-1} for the C-C stretch and torsion, respectively. Removal of the π electron allows the two methylenes to twist ~15° to relieve repulsions present in the neutral.[47] Whether the analogy with ethylene is appropriate in this case is uncertain, owing to a lack of theoretical and experimental information.

Assignment of the observed progression in allyl cation is hindered by the absence of data concerning the vibrations of the radical and isotope effects on the first photoelectron band. It can be suggested, however, that the arguments presented for benzyl cation may apply to allyl cation owing to the similarity of the interaction of the unpaired π electron with the rest of the π system in both species.

Conclusion

In addition to providing ionization potentials and heats of formation, the first photoelectron bands of allyl and benzyl radicals obtained in these experiments have yielded new information regarding the nature of the unpaired electron. In benzyl radical, this electron is nonbonding or slightly bonding. The vibrational spacing of its photoelectron band changes on isotopic substitution, indicating that the electron is mainly localized on the exo methylene. This is consistent with spin densities derived from ESR experiments. Calculations on allyl radical have shown its unpaired electron to be mainly nonbonding, and the lack of change in geometry on formation of the cation is consistent with this.

The striking similarity in shape of the first photoelectron bands of allyl and benzyl radicals suggests that the interaction of the ejected electron with the remaining π electrons in both radicals is similar. The question arises as to whether this might be the case for all conjugated π-type radicals. There is evidence, for example, that cycloheptatrienyl radical undergoes no change in geometry on formation of the cation.[48] Photoelectron spectroscopic studies will no doubt contribute much toward clarification of this problem, providing information on the interaction of the unpaired electron with substituent groups, and on the importance of the location of the radical center with respect to the rest of the π system.

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