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Photoelectron Spectroscopy of Methyl, Ethyl, Isopropyl, and *tert*-Butyl Radicals. Implications for the Thermochemistry and Structures of the Radicals and Their Corresponding Carbonium Ions

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Abstract: The first photoelectron bands of the series of simple alkyl free radicals CH_3, CH_3CH_2, CH_3CD_2, CH_3CHCH_3, and $C(CH_3)_3$ have been obtained. The adiabatic and vertical ionization potentials, respectively, are 9.84 ± 0.02 eV for methyl radical, 8.39 ± 0.02 and 8.51 ± 0.02 eV for ethyl radical, 8.38 ± 0.02 and 8.50 ± 0.02 eV for ethyl-*1,1*-d_2 radical, 7.36 ± 0.02 and 7.69 ± 0.02 eV for isopropyl radical, and 6.70 ± 0.03 and 6.92 ± 0.03 eV for *tert*-butyl radical. The heats of formation of the corresponding carbonium ions are calculated to be 261.8 ± 0.5 kcal/mol for methyl cation, 219.2 ± 1.1 kcal/mol for ethyl cation, 187.3 ± 1.1 kcal/mol for isopropyl cation, and 162.9 ± 1.2 kcal/mol for *tert*-butyl cation. The implications of these data for the gas-phase proton affinity scale are explored. Band structure is resolved, and possible assignments are presented. The results are discussed in terms of the interactions of methyl groups with trigonal carbon radical and ion centers.

Introduction

Methyl groups bonded to a radical or positive ion center exert a profound influence on both structure and stability of the trigonal site. However, the nature and magnitude of the interactions involved differ markedly in the neutral and charged species. Photoelectron spectroscopy offers a means of probing these substituent effects in a direct way. The extent to which nuclear coordinates and force constants of the equilibrium ion and radical structures differ is reflected in the Franck-Condon envelope of the first photoelectron band. For example, consider the case of CH_3, the simplest alkyl radical. Removal of the unpaired electron to form CH_3^+ primarily affects the force constant of the out-of-plane bending coordinate,[1,2] as shown schematically in Figure 1. Both radical and ion are planar, and the first photoelectron band[3,4] reflects this by mainly consisting of a single sharp peak. The force-constant change produces small Franck-Condon factors for transitions to higher vibrational levels, with the selection rule restriction that $\Delta v = 2$. This rather simple situation changes markedly when methyl groups are substituted to form CH_3CH_2, CH_3CHCH_3, and $C(CH_3)_3$, and the first photoelectron bands of these radicals reflect these changes. In addition, ionization potentials taken together with heats of formation provide quantitative information on relative stabilities. When considered along with results of other experimental and theoretical studies, the photoelectron data allow a better understanding of the effects of methyl substitution in alkyl radicals and ions.

Previous studies utilizing electron spin resonance (ESR) have probed the interaction of methyl groups with the unpaired electron on a carbon-centered radical. Electron spin densities can be derived from observed hyperfine splitting constants. The spin density on the radical center is found[5] to decrease in the order $CH_3 > CH_3CH_2 > CH(CH_3)_2 > C(CH_3)_3$. This trend is explained by the constraints on the unpaired electron to be orthogonal to the C-H orbitals of the same symmetry.

Extensive ESR studies have considered the effect of substituents on the conformations of radical centers. Electronegative substituents such as F and O are known to induce bending toward a pyramidal geometry. The mechanism for this is debated, however, and probably involves a combination of inductive and conjugative interactions.[6-8] The question remains as to whether CH_3 substituents also induce nonplanarity in radicals, and to what extent.[9-14]

Optical[15] and electron spectroscopy[3,4,16] have established that methyl radical is essentially planar. These results are supported by large basis set, configuration interaction calculations, which indicate that the out-of-plane bending coordinate has a single minimum.[1,2] Substitution of CH_3 for H to form CH_3CH_2 does not appear to change this situation appreciably. ESR data reveal essentially free rotation about the C-C bond,[5] consistent with a nearly planar trigonal carbon.[17] A Hartree-Fock geometry optimization using a large basis set[18] showed the radical center to be bent 6° out of plane. The two methyl groups in isopropyl radical are also freely rotating.[5]

The center of controversy rests on *tert*-butyl radical. Studies of the temperature dependence of the ^{13}C hyperfine splittings[12,13] indicate that the radical is nearly tetrahedral, with

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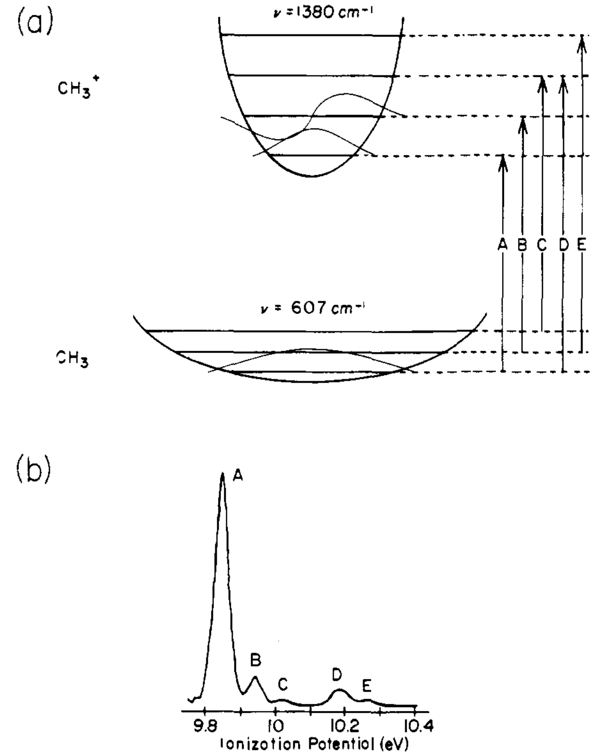

Figure 1. Schematic illustrating how changes in the out-of-plane bending potential give rise to the observed photoelectron spectrum for CH_3. (a) Potential curves for CH_3 and CH_3^+; the minima are at 0° (planar). Selection rules require that $\Delta v = 0,2$. (b) Observed photoelectron spectrum (taken from ref 3). Transition assignments are indicated. The experimental Franck-Condon factors are consistent with 500 K methyl radicals.

a barrier to inversion of 500-600 cal. This disagrees with views[11,14] that the deviation from planarity can be attributed purely to a medium effect. It has since been shown that medium effects are important,[19] but that even in a liquid medium *tert*-butyl radical is bent by 11° with a barrier to inversion of 450 cal/mol. Theory is also equivocal. An STO-3G calculation assuming C_3 symmetry for the radical indicated the geometry to be pyramidal but not tetrahedral.[10] This is at variance with an earlier study,[11] also at the minimal basis set level, which examined deviations of up to 10° out of plane from an initial configuration having C_{3h} symmetry. This work showed the radical to be strictly planar.

Matrix isolation studies of characteristic infrared (IR) absorptions in alkyl radicals[20,21] have shown that both ethyl and isopropyl radicals may be taken to be nearly planar, the trigonal carbon having considerable sp^2 character. The out-of-plane bending frequencies are 607 (gas phase),[22] 541,[20] tentatively 375,[20] and <200 cm⁻¹ [12,13,20] for CH_3, CH_3CH_2, CH_3CHCH_3, and $C(CH_3)_3$, respectively. The observed trend toward lower frequencies is attributable to a mass effect accompanied by a small change in the force constants through the series.

Removal of the unpaired electron to form a carbonium ion induces several major changes in these species. Electron delocalization onto the positive center is unrestricted by the orthogonality constraints present in the neutral radical. The presence of the positive charge polarizes the electron distribution in addition to inductive effects already present. Forces which may tend to induce bending in the radicals are changed to produce carbonium ions generally acknowledged to be planar. ^{13}C NMR studies indicate that methyl substitution at a carbonium ion center produces upfield shifts.[23] It was postulated that the observed deshielding is due to a reduction in electron density because of withdrawal by the methyl groups. Although this interpretation may not be unique, it has been substantiated by semiempirical[23] and STO-3G calculations.[24] The theoretical work indicates that methyl groups withdraw electrons through the σ framework, but donate them through the π system, resulting in a net increase of positive charge on the center carbon in the series $CH_3CH_2^+ < CH_3CHCH_3^+ < C(CH_3)_3^+$. Charge density distributions are highly basis set dependent, so these conclusions should be viewed with caution.

Little experimental information is available on the structure of the alkyl carbonium ions. IR spectroscopy under stable ion conditions[25] resulted in frequency assignments for isopropyl and *tert*-butyl cations, confirming the ion centers to be planar. The bulk of the structural data on these species results from ab initio calculations. Minimal basis set geometry searches[24] on the classical ethyl cation, isopropyl cation, and *tert*-butyl cation show these species to have lowest energy structures of C_s, C_{2v}, and C_{3h} symmetry, respectively. However, in each case there are several conformers which differ only slightly in energy. Ethyl cation has been suggested to exist in a bridged form in addition to its classical form. The relative stabilities of these two forms are highly dependent on the basis set used and the level of the calculation.[26-29] The best calculation[29] performed to date involves a large basis and a CEPA-PNO treatment of electron correlation effects. In this study, the bridged ion is found to be more stable than the classical one by 7.33 kcal/mol.

It is to be expected that shifts in electronic distribution which alkyl radicals undergo on ionization will result in substantial geometry changes. The photoelectron spectra confirm this expectation and, as will be discussed below, reveal these changes to be quite complex.

Experimental Section

Instrumentation. The apparatus used in these experiments is a photoelectron spectrometer built in the Caltech shops, specifically modified to study the products of pyrolysis. It has been described in detail elsewhere.[30]

Materials. The free radicals studied in this work were produced by pyrolysis of the alkyl nitrites:

$$\begin{gathered} RCH_2ONO \rightarrow RCH_2O + NO \\ RCH_2O \rightarrow R + CH_2O \end{gathered} \tag{1}$$

where R = CH_3CH_2, CH_3CD_2, CH_3CHCH_3, and $C(CH_3)_3$. The nitrites were prepared from the corresponding alcohols using standard techniques.[31] The unlabeled alcohols were obtained from Aldrich.

1-Propanol-*2,2-d_2* was prepared from propionic acid-*2,2-d_2*, which was labeled by deuterium exchange in a basic medium.[32] Sodium propionate (0.225 mol) was dissolved in 100 g of D_2O, to which had been previously added 0.6 g of sodium metal. The solution was placed in a glass pressure bottle and heated to 150 °C in a stirred oil bath. During the following 19 days, the old D_2O was distilled off and replaced by fresh D_2O a total of four times. At the end of this period, an NMR analysis showed the 2 position to be 90 ± 5% labeled. This isotopic purity is quite adequate for photoelectron spectroscopy. The aqueous solution was then acidified and extracted with ether, and the acid was distilled. The acid was reduced to the alcohol by $LiAlH_4$, using standard techniques. Deuterium content was checked at every step, and remained at 90%. The overall yield was 35-40%.

Photoelectron Spectra. Pyrolysis spectra were obtained using both He I and Ne I radiation. Radicals were produced at several temperatures over the range 500-700 °C in order to more fully assess the importance of hot bands. The shape of the ethyl radical band was observed to vary slightly with temperature. The relative heights of the adiabatic and vertical peaks changed from 0.57 to 0.62 on going from 600 to 700 °C. While this change was small, it was entirely reproducible. Count rates for all radicals were ~60 s⁻¹. The energy scales were calibrated using the He Iα and He Iβ bands of CH_2O, NO, and Ar. The resolution for these experiments is 30-35 meV. As the reported ionization potentials[33] are the average of several determinations, a reasonable estimate of our error is ±0.02 eV, except for *tert*-butyl, where the error limits are ±0.03 eV. The relative spacings within

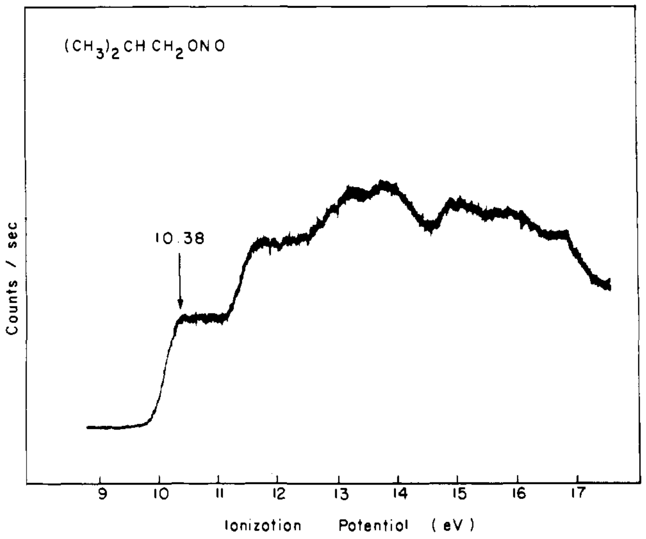

Figure 2. The He I spectrum of 2-methylpropyl nitrite.

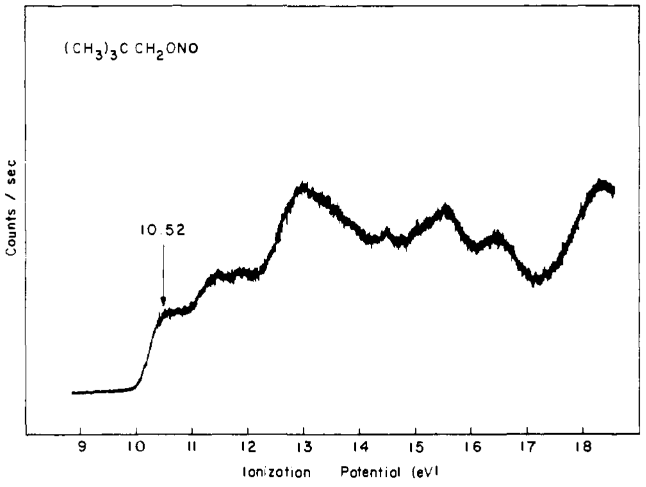

Figure 3. The He I spectrum of 2,2-dimethylpropyl nitrite.

each band are more highly reproducible, and are assigned error limits of ±0.005 eV.

Results

The spectra obtained in these experiments are presented in Figures 2-7. The ionization potentials (IPs) are summarized in Table I. In the remainder of this section, the data are discussed for the individual radicals, and compared to previous results.

Nitrites. The photoelectron spectra of 2-methylpropyl nitrite and 2,2-dimethylpropyl nitrite are presented in Figures 2 and 3. The spectrum of propyl nitrite has appeared elsewhere.[34] The vertical IPs of these species are 10.4, 10.5, and 10.7 eV, respectively.

CH_3. The methyl radical spectrum was obtained via the pyrolysis of azomethane. The results are in complete agreement with earlier photoelectron work,[3,4] and are not reproduced here. The first photoelectron band consists of a sharp peak at 9.84 eV followed by several very weak features at higher ionization energies. These features are mainly attributable to hot bands.

CH_3CH_2. The first photoelectron band of ethyl radical is shown in Figure 4a. A somewhat different spectrum of this species was reported in a preliminary communication.[34] Repetition of the early work using Ne I radiation showed that the feature assigned to be the adiabatic ionization potential was actually due to the He Iβ ionization of one of the NO bands.

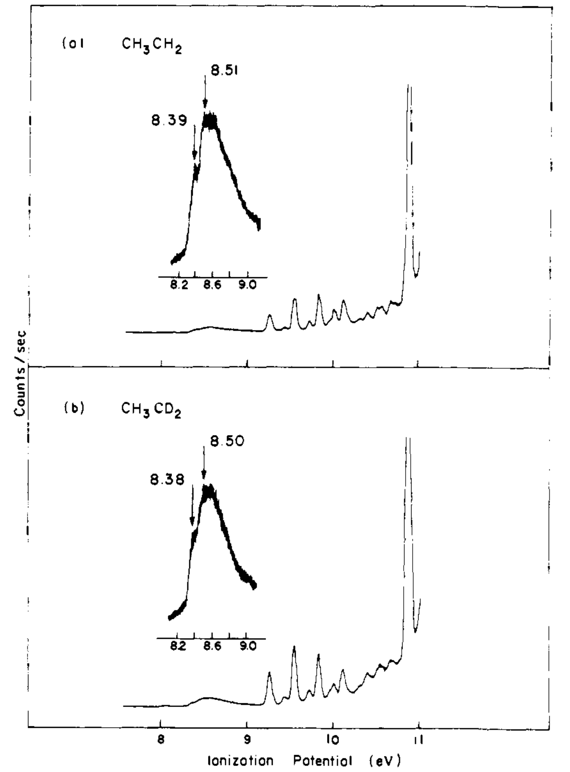

Figure 4. The Ne I spectra of ethyl radicals. Bands from 9.26 to 10 eV arise from Ne ionization of NO. CH_2O is at 10.884 eV. Inserts show the radical bands in greater detail. The main effect of the Ne I doublet is to broaden the peak maxima compared to those obtained with He I light. (a) The spectrum of ethyl radical. (b) The spectrum of ethyl-*1,1*-d_2 radical.

The current data, obtained under much higher resolution, gives adiabatic and vertical IPs of 8.39 and 8.51 eV, respectively. These values are in good agreement with electron impact IPs of 8.34[35] and 8.38 ± 0.05 eV,[36] an indirect measurement of 8.45 ± 0.2 eV,[37] and a photoionization IP of $\leq$ 8.4 eV.[38] The band has no resolved fine structure except for the two peaks chosen as adiabatic and vertical IPs.

CH_3CD_2. The spectrum of the partially deuterated ethyl radical, shown in Figure 4b, is qualitatively similar to that of the unlabeled species. The adiabatic and vertical IPs are 8.38 and 8.50 eV. They have not been determined previously.

CH_3CHCH_3. The first photoelectron band of isopropyl radical is shown in Figure 5. The adiabatic and vertical IPs are determined to be 7.36 and 7.69 eV, respectively. Since the band does not have a clear maximum, the most intense feature was chosen to be the vertical IP. Previous electron impact measurements have yielded values of 7.57[35] and 7.55 ± 0.05 eV.[36] Photoionization studies[38] gave an IP of <7.5 eV, with an upper limit to the adiabatic IP of 7.26 eV. The earlier electron impact studies are much closer to the vertical than the adiabatic value. Fine structure involving two characteristic energy spacings is resolved. The structure on the low ionization energy side of the band has a spacing of 0.09 eV (730 cm^{-1}). That found on the high ionization energy side has a spacing of 0.12 eV (970 cm^{-1}).

$C(CH_3)_3$. The data obtained for *tert*-butyl radical are presented in Figures 6 and 7. The vertical IP is found to be 6.92 eV. A previous electron impact determination gave an IP of 6.93 ± 0.05 eV.[36] Both values are in good agreement with vertical IPs of 6.95 ± 0.05[4a] and 6.90 ± 0.01 eV[39] which resulted from two other photoelectron spectroscopic studies of *tert*-butyl radical. The only previous measurement of the adiabatic IP of this species gave a value of 6.58 ± 0.01 eV.[39] In those experiments, the radicals were produced by pyrolysis at

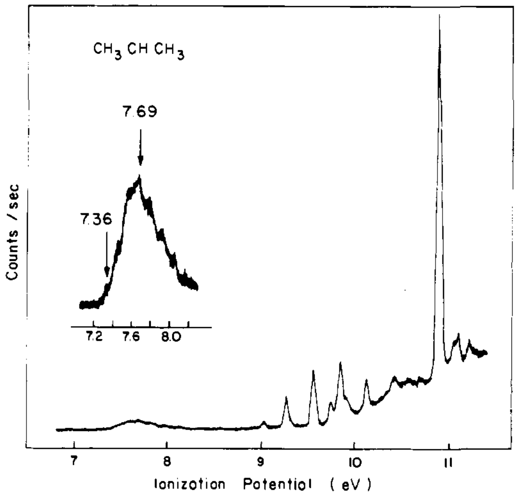

Figure 5. The He I spectrum of isopropyl radical. CH_2O, NO, and propylene are also present. The insert shows the radical band in greater detail.

Table I. Summary of Ionization Potentials[a]

radical	ionization potential, eV	
	adiabatic	vertical
CH_3	9.84	9.84
CH_3CH_2	8.39	8.51
CH_3CD_2	8.38	8.50
CH_3CHCH_3	7.36	7.69
$C(CH_3)_3$	6.70	6.92

[a] All IPs are ±0.02 eV, except for those of *tert*-butyl radical, which are ±0.03 eV.

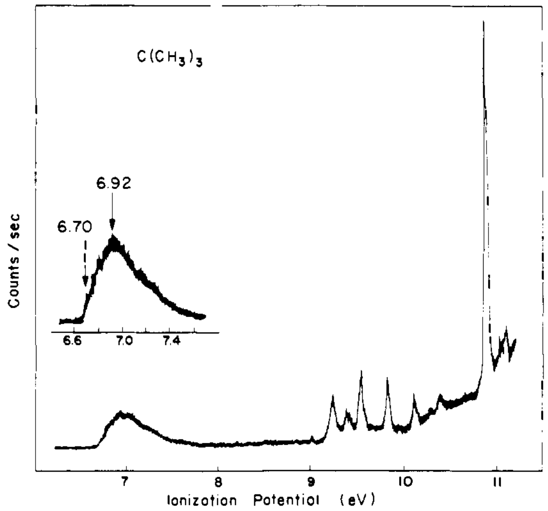

Figure 6. The He I spectrum of *tert*-butyl radical. CH_2O, NO, and isobutylene are also found in the spectrum. The insert shows the radical band in greater detail.

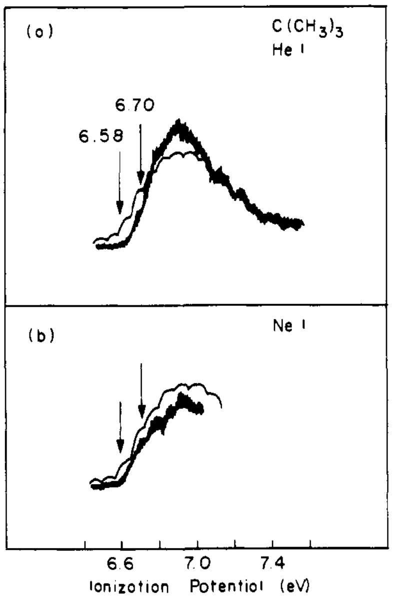

Figure 7. Comparison of our *tert*-butyl spectrum with the higher temperature Ne I spectrum from ref 39 (smooth curve). The adiabatic IP from the present work is 6.70 eV, while that of ref 39 is 6.58 eV. Hot bands can account for the discrepancy. (a) Overlay with the He I data of this work. (b) Overlay with the Ne I results of this work.

730 °C of 2,2′-azoisobutane heavily diluted with helium. In contrast, the radicals for the present work were generated at much lower temperatures (500–600 °C) using neat starting material. Comparison of our work to the earlier spectrum is shown in Figure 7. It can be seen that hot bands, which Jonathan and co-workers identified in their spectra, are present to a lesser extent (if at all) in the low-temperature data. Moreover, the band at 6.58 eV is missing in the spectra in Figure 7, although it appears to grow in at ≳650 °C. On the basis of these results, the adiabatic IP of *tert*-butyl radical is reassigned to be 6.70 eV.

Both previous photoelectron experiments showed evidence for fine structure on the first band, which was interpreted in terms of two separate vibrational progressions. As in the case of isopropyl radical, the lower energy spacing, 410[39] to 460 cm^{-1},[4a] is on the low ionization energy side of the band, and the higher energy spacing, 760[39] to 800 cm^{-1},[4a] is on the high ionization energy side. Fine structure was not clearly resolved when He I light was used in the present work. However, using Ne I radiation, a progression of ~450 cm^{-1} appeared (see Figure 7b). The structure on the high ionization energy side of the band was obscured by overlapping of spectra arising from the two Ne I lines.

Discussion

As noted in the Introduction, both theory and experiment indicate that successive CH_3 substitution in methyl radical is expected to profoundly affect the structure of that molecule. In addition, similar substitutions in methyl cation produce effects which cannot be directly compared to those in the neutral species. The photoelectron data illustrate this point in a dramatic way. While the CH_3 spectrum consists mainly of a sharp peak, indicative of essentially no geometry change on ionization of this radical, the ethyl, isopropyl, and *tert*-butyl radicals show evidence for significant and complex changes in nuclear coordinates and force constants. These changes make identification of adiabatic IPs difficult because of small Franck-Condon factors for the 0-0 transitions. Thus, as noted above, there are significant disagreements between previous studies utilizing threshold measurements and the present results. The data will be discussed in three parts. The first will reevaluate radical and carbonium ion stabilities in light of the adiabatic IPs reported here. The second will address itself to the problem of structure. The third will discuss the implications of isotope labeling experiments.

Thermochemistry. The heats of formation of alkyl carbonium ions can be calculated using adiabatic ionization potentials and heats of formation of the corresponding free radicals. It is evident that the ionic heats of formation are limited in accuracy by the radical heats of formation on which they are based. Over the years, the radical data have tended to con-

Table II. Summary of Free-Radical Heats of Formation[a]

R·	ΔH_f(R·)	R·	ΔH_f(R·)
CH_3	34.9[b]	$C(CH_3)_3$	6.8[c]
			8.2[f]
CH_3CH_2	25.7[c]		8.4[d]
	28.5[e]		9.3[g]
CH_3CHCH_3	17.6[c,d]		9.5[h]
	20.5[e]		12.1[e]

[a] All quantities in kcal/mol. Error limits are ±1–2 kcal/mol. [b] Reference 62. [c] Reference 40. [d] Reference 41. [e] Reference 42. [f] Reference 47. [g] Reference 63. [h] Reference 64.

Table III. Recommended Thermochemical Data[a]

R	ΔH_f-(R·)	ΔH_f-(R^+)[b,c]	PA-(olefin)[c,d]	$D(R^+–H^-)$[c,e]
CH_3	34.9	261.8		313.9
CH_3CH_2	25.7	219.2	159.0	274.1
CH_3CHCH_3	17.6	187.3	183.3	246.8
$C(CH_3)_3$	8.4	162.9	198.5	230.0

[a] All values in kcal/mol at 298 K. [b] Error limits ±1.1 kcal/mol for ethyl and isopropyl, ±1.2 kcal/mol for *tert*-butyl, and ±0.5 kcal/mol for methyl. [c] All heats of formation are calculated using the convention in ref 65, where the heat of formation of an electron at rest is taken to be zero at all temperatures. This convention gives $\Delta H_f(H^+) = 365.7$ kcal/mol and differs from the convention used in the JANAF Tables (ref 66). [d] Calculated using olefin heats of formation from ref 46 and $\Delta H_f(H^+) = 365.7$ kcal/mol, ref 65. [e] Calculated using alkane heats of formation from ref 46 and $\Delta H_f(H^-) = 34.7$ kcal/mol, ref 65.

verge[40,41] (see Table II). However, recent work[42] has yielded values revised upward from the earlier determinations. In order to assess the accuracy of the radical data, the adiabatic IPs can be combined with ionic heats of formation obtained in ion cyclotron resonance (ICR) studies. In particular, the case of *tert*-butyl cation will be examined closely, since its heat of formation has been assumed as a reference standard in the proton affinity scale.[43]

The ionic equilibria[44,45]

$$C_7H_7^+ + (CH_3)_3CCl \rightleftharpoons (CH_3)_3C^+ + C_6H_5CH_2Cl \quad (2)$$

$$C_7H_7^+ + (CH_3)_3CBr \rightleftharpoons (CH_3)_3C^+ + C_6H_5CH_2Br \quad (3)$$

which yield reaction enthalpies of −0.03 ± 0.24[44] and −1.25 ± 0.1 kcal/mol,[45] respectively, have been studied in ICR experiments. Taking $C_7H_7^+$ to be benzyl cation, which has a heat of formation of 211.0 kcal/mol,[30] and using literature heats of formation for the neutral species,[46] the heat of formation of *tert*-butyl cation is calculated to be 162.8 (from eq 2) and 161.0 kcal/mol (from eq 3). The largest sources of uncertainty in these calculations are the heats of formation of the benzyl halides. Even so, the two values are in remarkably good agreement with each other. Using these two values for $\Delta H_f(C(CH_3)_3^+)$, the heat of formation of *tert*-butyl radical is calculated to be 8.3 and 6.5 kcal/mol, respectively. The higher of the two numbers is in excellent agreement with results of Benson and Golden,[41,47] which give values of 8.4 and 8.2 kcal/mol, respectively.

In light of the results for the *tert*-butyl system, it seems likely that the higher radical heats of formation[42] should be viewed with caution. Accordingly, best values for free-radical and carbonium ion heats of formation resulting from this work are presented in Table III. Proton affinities of the corresponding olefins and heterolytic bond dissociation energies of the corresponding alkanes are also given. The major change in carbonium ion heats of formation is for $\Delta H_f(C(CH_3)_3^+)$, which is 6.1 kcal/mol below the previous accepted value.[43] This new value gives the proton affinity (PA) of isobutene as 198.5 kcal/mol, which can be combined with the proton affinity difference between isobutene and ammonia to obtain the PA of the latter species. Two values for this difference have been obtained by Kebarle (8.1 kcal/mol)[43] and Taft (8.8 kcal/mol),[48] by measuring free energies for proton transfer equilibria from several species (including acetone) to isobutene, and estimating the appropriate entropy term. The apparent discrepancy between the two numbers can be removed by using the results of a study by Ausloos and Lias[49] in which the entropy correction for equilibrium transfer of a proton between isobutene and acetone was measured directly. They showed that the enthalpy change for proton transfer from *tert*-butyl cation to acetone is −1.5 kcal/mol. The results of Taft[48] and Kebarle[43] lead to a value of $\Delta H = -8.4$ kcal/mol for proton transfer between acetone and ammonia. Combining the two enthalpies, a proton affinity difference of −9.9 kcal/mol is obtained for isobutene and ammonia, which, using the data in Table III, yields $PA(NH_3) = 208.4$ kcal/mol. Alternatively, the proton affinity difference between propylene and ammonia, determined to be 20.0 kcal/mol,[43] can be used to give $PA(NH_3) = 204.1$ kcal/mol. This is somewhat less than the isobutene results. Condensation reactions in propylene make this system less tractable for studies of proton-transfer equilibria, however, and more weight should be given the isobutene results. Finally, an independent measure of $PA(NH_3) = 203.6 \pm 1.3$ kcal/mol has recently been made in photoionization studies of ammonia dimers.[50] Because of the difficulty of picking an onset to a gradually rising curve, the photoionization value may be considered to be a lower limit to the true PA.

Aspects of Ion and Radical Structures. A striking feature of the first photoelectron bands of ethyl, isopropyl, and *tert*-butyl radicals is their relatively smooth shape. When vibrational progressions are resolved, they appear only weakly. This is indicative of excitation of several vibrational modes of the ion upon its formation. In the absence of dramatically higher instrumental resolution and very accurate structural and force field calculations, the Franck-Condon envelopes can only be used to obtain qualitative information regarding geometry changes on ionization.

As noted in the Introduction, methyl radical undergoes essentially no geometry change on ionization. Its photoelectron spectrum exhibits a double quantum transition in the out-of-plane bending mode, ν_2, indicating that a planar radical is becoming a planar ion.[3] The frequency of the ν_2 mode is much larger in the ion (1380 cm^{-1})[3] than in the neutral (607 cm^{-1}).[22] Thus, the curvature of the ionic potential surface is higher than that of the neutral. Substitution of a CH_3 group to form ethyl radical is calculated to displace the minimum energy geometry of the radical center away from 0° (planar). In addition, theoretical considerations indicate that bond pair repulsions as well as repulsive or attractive interactions of the unpaired electron with C–H and C–C bonds around it produce a potential energy surface having multiple minima separated by low barriers ($\lesssim$200 cal/mol).[18,51] The degree of freedom linking these minima is a combined out-of-plane bend and torsion about the C–C bond. Calculations show that the ion, on the other hand, can assume either a rather rigid, bridged structure[26-29] or one of several planar classical structures separated by barriers similar in height[24] to those of the radical. Recently, a calculation has been made of the relative energies of the two forms, and of the energy profile for their interconversion.[29] No barrier is found to the motion of a hydrogen atom from a terminal to a bridging position, so the classical structure does not correspond to a local minimum in the potential energy surface.

The first photoelectron bands of ethyl and ethyl-*1,1*-d_2 radicals have two distinguishable peaks on their low ionization energy sides. No other prominent, regular features could be

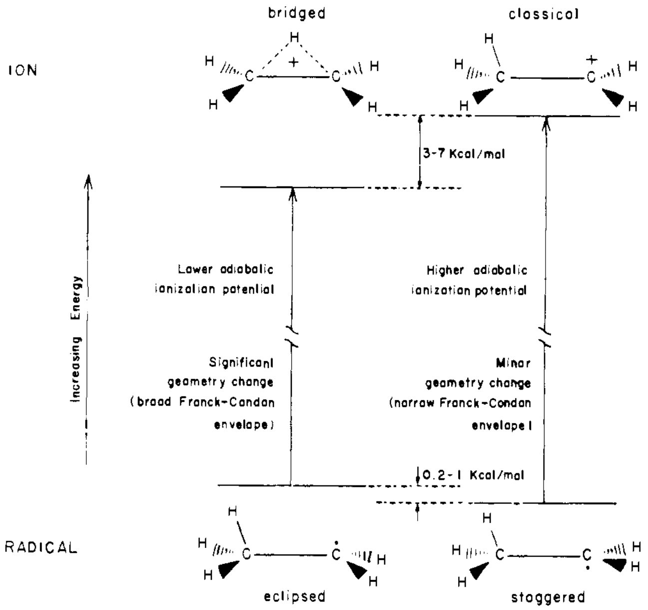

Figure 8. Schematic of the various forms of the ethyl cation and radical that may be important in the photoelectron spectrum of the ethyl radical. (See text.)

resolved. The separation between the peaks (identified as the adiabatic and vertical IPs) is unaffected by deuterium substitution. Transitions from a classical radical to the classical form of the ion are expected to be the most probable ones. Transitions to the bridged form should be less intense, since they involve constraints in two coordinates: the position of the bridging hydrogen and the torsional angle of the CH_2 group relative to the CH_3 group. Thus, there are two possible assignments for the photoelectron band. The first possibility assumes that Franck-Condon factors for transitions to the bridged ion are small, so that the band shape mainly reflects the overlap of classical structures having C_s symmetry at most. The two peaks would thus correspond to a progression in a combined C-C stretch and CH_3 deformation motion, analogous to isopropyl and *tert*-butyl radicals, as discussed below. Torsions about the C-C bond are also expected to be excited because of the expected change in degree of planarity of the trigonal carbon center.[18,51] Superposition of a low-frequency torsional progression on a 0.12-eV progression and (possibly) a low-intensity, broad envelope for transitions to the bridged ion would produce a smooth band shape, as is observed. It should be noted that, *if* this assignment is correct, the true adiabatic ionization potential has not been determined in this work.

The second possible interpretation of the ethyl spectrum assumes that the bridged ion is more stable. The peak identified as the adiabatic IP would then correspond to a transition to this lowest energy structure of the ion from that conformation of the radical most closely resembling it. The vertical transition would be to the classical form of the ion, which is closer to the structure of the radical. The remainder of the band would involve transitions from other conformations of the radical to both ionic structures. A schematic illustrating this possible assignment is shown in Figure 8. The energy difference between the adiabatic and vertical IPs would be approximately that of the two forms of the ion, since the rotational conformers of the radical are expected to be quite close in energy. This quantity is ~3 kcal/mol. The calculated energy difference of 7.33 kcal/mol[29] is in fair agreement with this experimental estimate if the zero-point energy difference between the two ionic structures is taken into account.

Experimental measures of the relative stabilities of the bridged and classical ethyl cations are sparse. In solution, isotopic hydrogen scrambling has been observed, with an activation energy of $\lesssim 1.9$ kcal/mol.[52] Gas-phase radiolysis, photoionization, and electron-impact experiments also showed evidence for extensive scrambling,[53] with an energy barrier $\lesssim 5$ kcal/mol.[54] Thus, experimentally, an activation energy is required for the scrambling process, which involves interconversion of classical and bridged forms for the cations. This barrier may just correspond to the energy difference between the two structures. It is also possible that an additional barrier exists along one of the coordinates involved in the H-transfer process. Calculations[29] indicate that no barrier is present along the H-bridging coordinate, but other motions involved in the scrambling (e.g., rotation of the CH_3 group in the open structure) were not examined.

It is clear that calculations of Franck-Condon factors in both the hydrogen-bridging and internal rotation coordinates are necessary to decide whether the photoelectron results can be expected to probe only one or both forms of the cation. Studies over a range of 200 °C showed the adiabatic peak to increase in intensity relative to the vertical as temperature increased, indicating that the radicals may comprise several populations in equilibrium with each other. Unfortunately, owing to the small changes involved, the data were not definitive. No evidence for vibrational hot bands was found.

In contrast to the ethyl cation, neither isopropyl[55] nor *tert*-butyl[56] radicals have low-lying hydrogen-bridged structures. The photoelectron bands of both species exhibit structure interpretable as two distinct progressions: a low-frequency one on the low ionization energy side of the band and a higher frequency one on the high ionization energy side of the band. Both sets of radicals and ions are expected to have a number of conformations linked, as in the case of ethyl radical, by combined torsional and out-of-plane motions. It is interesting that, despite the large numbers of structures involved, the band shapes can be rationalized in terms of single rigid forms for the radical and its ion.

The first photoelectron band of *tert*-butyl radicals has been reported previously.[4,39] Dyke et al. analyzed the fine structure of the band in some detail. Two progressions were observed, and assigned on the basis of a normal coordinate analysis and IR experiments in solution.[25] The 460-cm^{-1} progression was assigned to an out-of-plane bend, and the 760-cm^{-1} progression to a symmetric C-C stretch. These results were found to be most consistent with a nonplanar radical forming a planar ion. Assuming the adiabatic IP to be 6.58 eV, a barrier to inversion and out-of-plane angle were estimated for the radical. This barrier height of 900 ± 100 cm^{-1} is in disagreement with the results of ESR experiments, which yield a barrier of $\lesssim 160$ cm^{-1}. Use in the analysis of the higher adiabatic IP measured in this work would lower the barrier somewhat.

Although isopropyl radical and cation are expected to have C_{2v} as their highest symmetry, consideration of the various rotational conformations of the CH_3 groups together with C-H and C-C bond pair repulsions[51] leads to a more reasonable assumption of C_s symmetry or less. Thus, selection rules for vibrational excitation in the ion will allow modes of a′ symmetry in C_s, or all modes in the case of C_1 symmetry.[57] A normal coordinate analysis for isopropyl cation under C_{2v} symmetry has been performed.[25] The a_1 and b_2 modes are totally symmetric a′ modes under C_s symmetry. Therefore, at least modes of the a_1 and b_2 representations can be observed. An absorption at 930 cm^{-1} has been recorded in solution, and assigned to be a mixed, totally symmetric C-C stretch, C-H bending mode (calculated at 892 cm^{-1}).[25] This is very close to the gas-phase value of 970 cm^{-1} determined in the present work. Assignment of this mode to a skeletal deformation parallels the assignment made in the case of *tert*-butyl cation.[39] Of all 24 calculated frequencies, that closest to the observed progression of 730 cm^{-1} is 670 cm^{-1}. Although this b_2 mode is not assigned in ref 25, it probably corresponds to an out-of-plane deformation about the ion center, based on extrapolations using known frequencies for this vibration in CH_3^+ [3] and $C(CH_3)_3^+$.[39] This assignment also parallels that made in the case of *tert*-butyl cation.[39]

It should be noted that, even if the isopropyl and *tert*-butyl radicals are nearly planar, dramatic differences in curvature of the out-of-plane potential energy surfaces between the radicals and their ions will result in excitation of out-of-plane vibrations.[57] That these differences do exist is illustrated by comparing the out-of-plane bending frequencies in CH_3 and CH_3^+ (607[22] and 1380 cm^{-1} [3]) and $C(CH_3)_3$ and $C(CH_3)_3^+$ (<200[12,13,20] and 347-460 cm^{-1} [39]).

Isotope Effects on the Ionization Potentials. Isotope data exist for two of the radicals discussed here. The IP of CH_3 is 9.840 eV, while that of CD_3 is 9.831 eV.[3] The adiabatic IP of CH_3CH_2 is 8.39 eV, compared to CH_3CD_2, which has a value of 8.38 eV.[58] These isotope shifts can be interpreted in terms of an overall change in curvature of the radical potential energy surface on ionization.[30] If deuterium substitution lowers the IP, the unpaired electron has antibonding character in the radical. This is the case for methyl radical, and can be illustrated by the large increase in its out-of-plane bending frequency on ionization. The unpaired electron in ethyl radical also has antibonding character overall. This electron, unlike that in methyl radical, has both π- and σ-type interactions with the rest of the radical. It is unknown at present which type of interaction dominates, or whether both interactions are antibonding.

Conclusions and Commentary

Vertical and adiabatic IPs for CH_3, CH_3CH_2, CH_3CD_2, CH_3CHCH_3, and $C(CH_3)_3$ have been determined in this work. They have been used to calculate thermochemical data for the corresponding ions, such as heats of formation, absolute proton affinities of the alkenes, and heterolytic bond dissociation energies of the alkanes. As a result of the present experiments, the proton affinity of NH_3, an important reference standard, has been revised upward from its old value of 202.0 kcal/mol to 208.4 kcal/mol. Reasonable error limits are ±2 kcal/mol. Additional experiments are underway in our laboratory to verify this result.

In contrast to methyl radical, which undergoes no significant geometry change on ionization, the methyl-substituted radicals incur complex geometry changes, with excitation of several vibrational modes. This situation is partly the result of very low barriers to internal rotation and out-of-plane bending in both the ions and the neutrals. Consequently, quantitative analysis of the Franck-Condon envelopes of the photoelectron bands of these radicals is very difficult. Deconvolution of the vibrational progressions present cannot always be done in a unique manner. In view of this, photoelectron data cannot yet be cited as evidence for the planarity or nonplanarity of alkyl radicals having low symmetry, contrary to recent suggestions made in the literature.

That the observed band shapes are attributable in part to the excitation of complex molecular motions is confirmed by recent work in our laboratories on sterically rigid species such as 2-norbornyl.[59] The first photoelectron band of this radical exhibits sharp, well-resolved structure, and little evidence for geometrical rearrangement on ionization. This is not found for the cyclopentyl and cyclohexyl monocyclic radicals, whose band shapes are broad and featureless.[60]

Deuterium labeling has shown that the unpaired electron in both methyl and ethyl radicals is antibonding. Isotope data are not available for isopropyl and *tert*-butyl radicals. However, excitation of symmetric C-C stretches and C-H bends in both species on ionization indicates a substantial redistribution of electron density in forming the ion from the radical.

The present work is not inconsistent with recent theoretical calculations[29] on the bridged and open forms of ethyl cation, provided that some assumptions are made concerning which regions of the potential energy surface are being probed. If both structures are being formed, then the calculated energy difference of 7.33 kcal/mol is high in comparison to the 3 kcal difference between adiabatic and vertical ionization energies. Additional theoretical and experimental work is necessary to choose between several possible interpretations of the data.

It is interesting to compare the first photoelectron bands of the aliphatic alkyl radicals with those of the conjugated π-type radicals allyl,[30] benzyl,[30] and cycloheptatrienyl.[61] The latter three all have similar features: the adiabatic and vertical ionization potentials coincide, well-resolved vibrational progressions are observed, and the bands are relatively narrow. It appears that relaxation of the pure π character of the unpaired electron may be a reason for the complexity and breadth of the photoelectron bands obtained in the present work. Steric rigidity is also a factor, as has been noted above, but even the strained radicals have fairly broad bands. Work is underway in our laboratory to investigate the relative importance of these factors. It is hoped that the experiments will lead to a better understanding of the role of π and σ character of the unpaired electron in radicals in determining the structure and reactivity of these species.

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A Photoelectron Spectroscopic–Molecular Orbital Study of SF_4 and Related Fluorosulfuranes

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Abstract: He(I) photoelectron spectra (UPS) are reported for SF_4, CF_3SF_3, $(CF_3)_2SF_2$, Me_2NSF_3, $(Me_2N)_2SF_2$, $F_3SCF_2SF_3$, and $(CF_3)_2S$. The UPS of SF_4 was interpreted on the basis of SCF-X_α scattered-wave (X_α SW) calculations in which the ionization energies (IEs) of all the valence molecular orbitals (MOs) were computed by the transition-state method. MNDO MO calculations have also been performed on SF_4. The observation that the F(2p) π-type orbitals are ~2 eV more stable in the equatorial than in the axial sites is consistent with a previous X-ray photoelectron spectroscopic study of SF_4. The UPS of the other fluorosulfuranes were interpreted using qualitative arguments and on the basis of empirical trends in the IEs. For all the fluorosulfuranes studied here a correlation was noted between the IE of the sulfur "lone-pair" MO and the sum of the group electronegativities of the equatorial substituents. A detailed discussion of the $7a_1$, $3b_1$, $4a_1$, $2b_2$, $2b_1$, and $3a_1$ MOs of SF_4 is presented from the standpoint of the X_α SW calculations. The HOMO ($7a_1$) involves approximately equal charge densities on the sulfur atom and each of the axial fluorine (F_a) ligands. The $3b_1$ MO features a modicum of bonding interaction between the axial and equatorial fluorine ligands. The orbital contour map for the $2b_1$ MO is reminiscent of the hypervalent three-center, four-electron model for F_a–S–F_a bonding.

I. Introduction

The sulfuranes are well-known examples of chemical systems in which the classical Lewis octet of the central atom is expanded. Dubbed "hypervalent" by Musher,[1] molecules of this general type have attracted the attention of both theoretical and structural chemists. From a practical standpoint, fluorosulfuranes play an important role as fluorinating agents[2] and as precursors for the synthesis of sulfonium cations.[3]

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