Photoelectron Spectroscopy of 1-Propyl, 1-Butyl, Isobutyl, Neopentyl, and 2-Butyl Radicals: Free Radical Precursors to High-Energy Carbonium Ion Isomers

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Abstract: The first photoelectron bands of 1-propyl, 1-butyl, isobutyl, neopentyl, and 2-butyl radicals have been obtained. Adiabatic and vertical ionization potentials, respectively, are 8.15 ± 0.02 and 8.43 ± 0.02 eV for 1-propyl radical, 8.02 (+0.04 − 0.1) and 8.50 ± 0.04 eV for 1-butyl radical, 7.93 (+0.03 − 0.1) and 8.31 ± 0.03 eV for isobutyl radical, 7.88 ± 0.05 and 8.25 ± 0.03 eV for neopentyl radical, and 7.25 ± 0.02 and 7.59 ± 0.03 eV for 2-butyl radical. From recently determined or estimated heats of formation of the radicals, heats of formation of the corresponding carbonium ions are calculated to be 210.5 ± 1.1 kcal/mol for 1-propyl cation, 201.9 ± 3 kcal/mol for 1-butyl cation, 197.9 ± 3 kcal/mol for isobutyl cation, 188.8 ± 2.3 kcal/mol for neopentyl cation, and 181.0 ± 1.1 kcal/mol for 2-butyl cation. The energetics of ion solvation processes are assessed from a comparison of the gas-phase results to solution data where these ions are generated as nascent products of ionization processes or are proposed as reaction intermediates in isomerization reactions. With the exception of the 1-propyl radical spectrum, the spectra exhibit no resolved vibrational structure. The possible origins of a weakly resolved 540 ± 160 cm^{-1} vibrational progression observed on the 1-propyl radical band are discussed. An analysis of these spectra, along with those of ethyl and 2-propyl radicals, reveals treads in ionization potentials that may be interpreted in terms of inductive and hyperconjugative effects of methyl substituents β to primary or secondary cation centers.

Carbonium ions have a great tendency, in the gas phase[1] and in solution,[2] to rearrange. The lowest energy isomer is often well characterized by spectroscopic studies of stable-ion solutions,[3] by calorimetric measurements,[4] and by gas-phase studies of ion fragmentation thresholds[5] and ion–molecule reactions.[6] Higher energy isomers are usually much more elusive and thus poorly characterized.

The present work is an extension of our earlier study, using photoelectron spectroscopy, of the most stable propyl and butyl carbonium ions, the 2-propyl and *tert*-butyl cations.[7] To study the higher energy carbonium ion isomers, the first bands of the photoelectron spectra of 1-propyl, 1-butyl, isobutyl, and 2-butyl radicals have been obtained. To complete the series in which the β-hydrogens of the ethyl radical are successively replaced with methyl groups, we have also studied the neopentyl radical. Since photoelectron band shapes are governed by Franck–Condon factors, the spectrum of a radical yields thermochemical and structural information relating to the cation, in a specific electronic state, with a geometry similar to that of the radical. Any isomerization of the cation *subsequent* to ionization will not affect the results since it is only the ejected electron that is analyzed. Examination of the ionization energetics of 1-propyl, 1-butyl, isobutyl,

neopentyl, and 2-butyl radicals has yielded the heats of formation of 1-propyl, 1-butyl, isobutyl, neopentyl, and 2-butyl cations, respectively, in their ground electronic states. Trends in ionization potentials have been interpreted in terms of inductive and hyperconjugative stabilization available to the ions in their nascent conformations.

Photoelectron spectroscopy of primary radicals offers a unique opportunity to study primary cations. Theoretical and experimental evidence suggests that primary alkyl cations are extremely transient species. The most detailed ab initio molecular orbital calculations[8] and semiempirical calculations[9,10] failed to determine a minimum on the $C_3H_7^+$ potential energy surface corresponding to 1-propyl cation. The majority of gas-phase experiments have revealed that 1-propyl, 1-butyl, isobutyl, and neopentyl cations isomerize either to a protonated cycloalkane or to a more stable secondary or tertiary isomer much more rapidly than they react.[1a,11-15] Attempts to trap 1-propyl cation, for example, have shown that it rearranges in less than 10^{-10} s.[1a,11] Accurate heats of formation of the primary cations studied in this work cannot be obtained by measuring thresholds for appearance of fragment ions[5] because isomerization of the precursor ion can occur either before or during dissociation.[16,17] The threshold then corresponds to formation of a more stable isomer.[5b,18] Attempts to prepare primary cations under stable-ion conditions for observation by NMR have been unsuccessful.[19] Deamination reactions are often used in solution to generate "free" cations which are characterized by their extensive rearrangement products.[20] Detailed studies

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using primary amines have revealed that the unrearranged primary products are not formed from totally free carbonium ion intermediates,[21] and thus the observation of such products may offer little information concerning the stability of truly free gas-phase primary cations.

Obtaining the photoelectron spectrum of 2-butyl cation completes our study of the $C_4H_9^+$ species which have radical-like structures. 2-Butyl cation has been studied previously in both stable-ion media and in the gas phase, since there is a significant barrier to rearrangement to its more stable isomer, *tert*-butyl cation.[11,12,22] Nevertheless, even in a matrix at -190 °C, 2-butyl cation is not a static secondary cation.[23] Olah,[24] Saunders,[25] and their co-workers have proposed that an equilibrium between a static nonclassical bridged species and a classical secondary cation, both close in energy, accounts for the NMR data on 2-butyl cation.

With the photoelectron spectroscopic studies of alkyl radicals such as methyl, ethyl, 2-propyl, and *tert*-butyl[7] as a foundation, where both the radical and cation have been well characterized, less well-understood systems such as those studied here can be examined. Assignments of the spectra of primary and 2-butyl radicals are assured since the spectra of the more stable secondary or tertiary radicals, which are possible rearrangement products of the radicals themselves, are either available or can be predicted with reasonable certainty. In addition to providing the desired spectra, photoelectron spectroscopy can also be used to follow both thermal decomposition and isomerization pathways of the radicals by identifying the spectra of products.[26] This is done in the present study, using elevated temperatures to increase the extent of radical decomposition.

Experimental Section

Photoelectron spectra were recorded on a spectrometer of standard design, which has been specifically modified to study products of gas-phase pyrolysis. It has been described in detail elsewhere.[27]

1-Propyl, 1-butyl, isobutyl, neopentyl, and 2-butyl radicals were produced by thermal decomposition of 1-butyl nitrite, 1-pentyl nitrite, 3-methyl-1-butyl nitrite, 3,3-dimethyl-1-butyl nitrite, and 2-methyl-1-butyl nitrite, respectively, according to reactions 1 and 2. The nitrites were

$$RCH_2ONO \rightarrow RCH_2O + NO \qquad (1)$$

$$RCH_2O \rightarrow R + CH_2O \qquad (2)$$
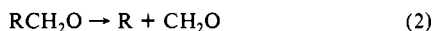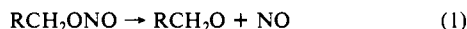
prepared by using standard procedures[28] from the corresponding alcohols obtained from Aldrich: 1-butanol, 1-pentanol, 3-methyl-1-butanol, 3,3-dimethyl-1-butanol, and 2-methyl-1-butanol, respectively. Pyrolyses were performed over the range 470–650 °C using a 2.2-cm-long pyrzolyzer. Since the pyrolyses are done at low pressures ($\sim 10^{-2}$ torr), molecules are heated by collisions with the wall of the pyrolyzer and there are few molecule–molecule collisions. Some unimolecular radical processes may, in fact, take place on the pyrolyzer wall. In an attempt to decrease the amount of secondary products and thereby increase the spectrum of the desired radical, a shorter pyrolyzer (0.8 cm) was used for some experiments. Regardless of which pyrolyzer was used, the hot gases traversed a 0.75-cm path after exiting the pyrolyzer and before intersecting the photon beam. Pyrolysis temperatures ~ 110–180 °C higher were necessary with the short pyrolyzer to obtain the same amount of precursor decomposition achieved with the long pyrolyzer. Spectra showing the same amount of precursor decomposition were compared, and no increase of the primary radical products nor decrease in the secondary radical products, relative to the amount of nitrite decomposition, was apparent. There is also no evidence that the slightly higher pyrolysis temperatures change the shapes of the radical spectra (due to a temperature-dependent

Table I. Summary of Alkyl Radical Ionization Potentials

R	ionization potential by photoelectron spectroscopy,[a] eV		ionization potential by electron impact,[b] eV
	adiabatic	vertical	
CH$_3$CH$_2$	8.39 ± 0.02	8.51 ± 0.02	8.38 ± 0.05
2-C$_3$H$_7$	7.36 ± 0.02	7.69 ± 0.02	7.55 ± 0.05
t-C$_4$H$_9$	6.70 ± 0.03	6.92 ± 0.03	6.93 ± 0.05
1-C$_3$H$_7$	8.15 ± 0.02	8.43 ± 0.02	8.10 ± 0.05
i-C$_4$H$_9$	7.93 (+0.03 – 0.1)	8.31 ± 0.03	8.01 ± 0.05
neo-C$_5$H$_{11}$	7.88 ± 0.05	8.25 ± 0.03	7.91 ± 0.05
1-C$_4$H$_9$	8.02 (+0.04 – 0.1)	8.50 ± 0.04	8.01 ± 0.05
2-C$_4$H$_9$	7.25 ± 0.02	7.59 ± 0.03	7.41 ± 0.05

[a] From this work except for CH$_3$, CH$_3$CH$_2$, 2-C$_3$H$_7$, and t-C$_4$H$_9$ from ref 7. [b] Values were obtained by using an energy-resolved electron beam from ref 18 except for neo-C$_5$H$_{11}$ from ref 29; the uncertainty in this value is assumed to be the same as reported for other electron impact values.

population of radical conformations or higher vibrational states). In particular, no hot bands were observed. We report the best spectra obtained with both pyrolyzers. Unless otherwise specified, pyrolysis temperatures refer to those for the long pyrolyzer.

Spectra were recorded using He I and in some cases Ne I radiation in order to determine those spectral features arising from the He Iβ ionization. Energy scales for the pyrolysis spectra were calibrated from the peaks due to NO and CH$_2$O, both products of the nitrite decomposition. Room-temperature spectra were calibrated using argon or xenon. Resolution for these experiments was 30–40 meV. Count rates at the radical band maxima for 1-propyl, 1-butyl, isobutyl, neopentyl, and 2-butyl radicals were ~ 26, 18, 27, 13, and 13 s^{-1}, respectively. Ionization potentials reported here are the average of several determinations. Reasonable estimates for the error involved in assigning an ionization potential (IP) to an identifiable part of a radical spectrum are ± 0.02 or 0.03 eV. In some cases it was necessary to choose an adiabatic IP for a photoelectron band with a slowly rising onset both obscured by another band, probably due to secondary radical products, and without vibrational structure. In this case, and when a vertical IP was chosen for a very broad band maximum, larger errors were assigned to the value.

Results

The ionization potentials measured in this work and, for comparison, values determined previously by electron impact using an energy-resolved electron beam[18,29] are presented in Table I.

Nitrites. The photoelectron spectra of 1-butyl nitrite, 1-pentyl nitrite, 3-methyl-1-butyl nitrite, 3,3-dimethyl-1-butyl nitrite, and 2-methyl-1-butyl nitrite are shown in Figure 1. The vertical IPs of these species are 10.4, 10.6, 10.6, 10.6, and 10.5 eV, respectively.

1-Propyl Radical. The Ne I spectrum of the first photoelectron band of 1-propyl radical is shown in Figure 2. The nitrite precursor was pyrolyzed at 615 °C by using the short pyrolyzer. At this temperature (corresponding to ~ 475 °C with the long pyrolyzer) the radical band is maximized, and small amounts of radical decomposition products are observed. The adiabatic and vertical IPs are 8.15 ± 0.02 and 8.43 ± 0.02 eV, respectively. The adiabatic IP is in good agreement with a previous electron impact value of 8.10 ± 0.05 eV[18] and a photoionization mass spectrometric estimate of ≤8.1 eV.[30]

With a He I lamp, the maximum of the radical band is at 8.37 ± 0.02 eV. Although a change in photoelectron band shape with lamp radiation energy cannot be ruled out, the apparent change in vertical IP is probably due to an impurity line in the He I lamp. Ionization of CH$_2$O by the He I$_\gamma$ line, which is 2.524 eV more

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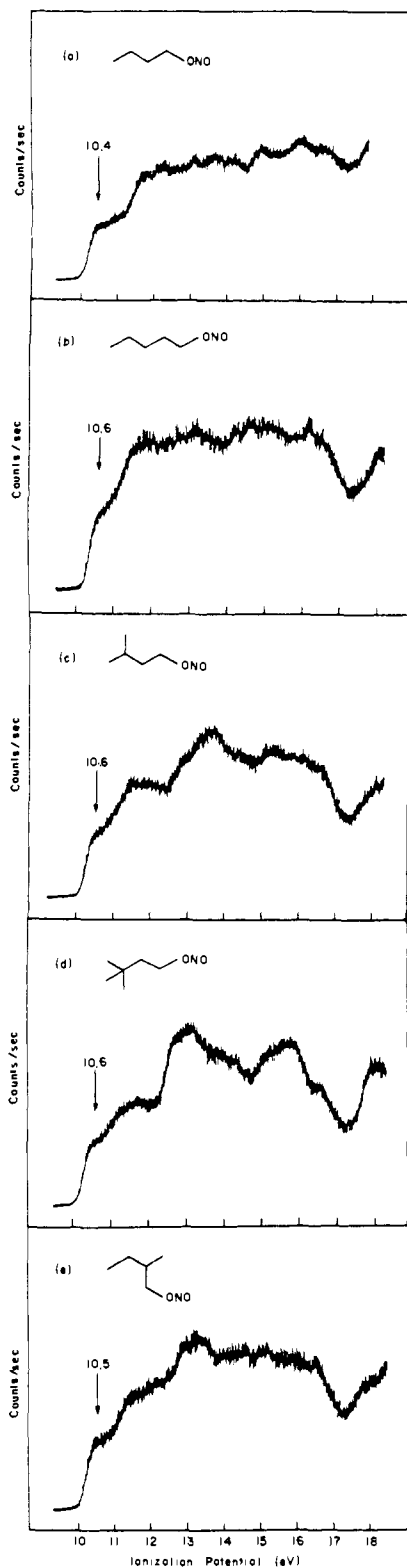(30) Elder, F. A.; Giese, C.; Steiner, B.; Inghram, M. *J. Chem. Phys.* **1962**, *36*, 3292.

PES of Radicals

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Figure 1. He I spectra of (a) 1-butyl nitrite, (b) 1-pentyl nitrite, (c) 3-methyl-1-butyl nitrite, (d) 3,3-dimethyl-1-butyl nitrite, and (e) 2-methyl-1-butyl nitrite.

energetic than the main He I_α line, would result in a photoelectron peak with an apparent IP of 8.360 eV. The He I_γ line is only 0.5% of the He I_α intensity, but given the low-intensity radical band and the high-intensity CH_2O He I_α peak, this impurity line is sufficiently intense to change the apparent vertical IP. Therefore, only the Ne I spectrum was used to assign the vertical IP.

A weakly resolved vibrational progression is just barely evident on the low ionization potential side of the band. The first and fifth peak of the progression correspond to the adiabatic and vertical ionization potentials, respectively. The five members of
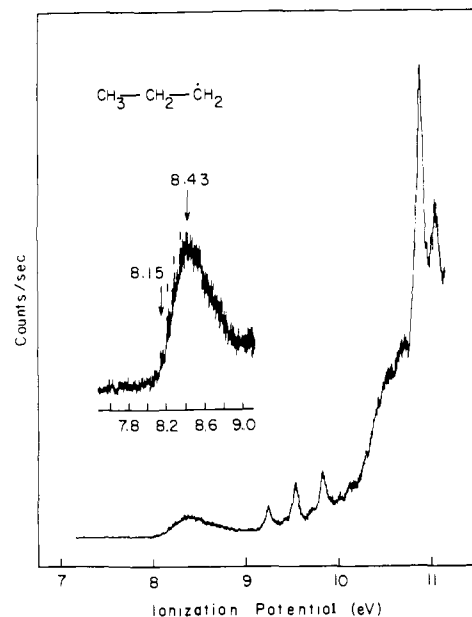

Figure 2. Ne I spectrum of 1-propyl radical and other products of the pyrolysis of 1-butyl nitrite. Peaks at 9.2–10, 10.5, and 10.9 eV arise from NO, ethylene, and CH_2O, respectively. Insert shows radical band in greater detail.
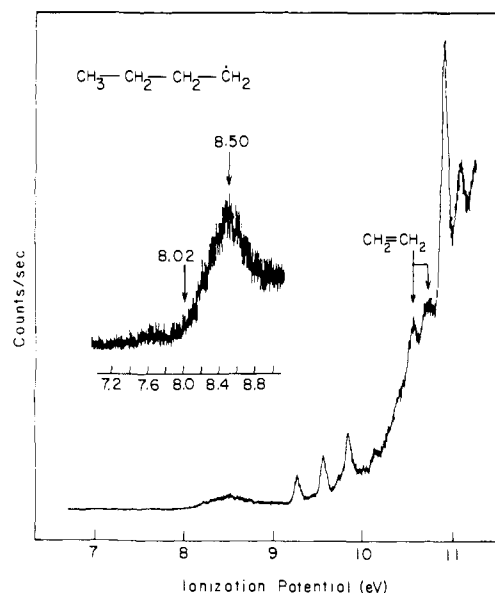

Figure 3. Ne I spectrum of 1-butyl radical and other pyrolysis products of 1-pentyl nitrite. Peaks at 9.2–10, 10.5, and 10.9 eV arise from NO, ethylene, and CH_2O, respectively. Insert shows 1-butyl radical band in greater detail. The very weak band just before the 1-butyl radical band is assigned to a secondary radical, possibly 2-butyl radical.

the progression are spaced by 0.067 ± 0.020 eV or 540 ± 160 cm^{-1}.

Above 500 °C significant amounts of ethylene at 10.51 eV[31] and methyl radical, which is accidentally coincident with a member of the NO progression at 9.84 eV,[32] are formed, and their production increases with temperature. At low (~470 °C) and high (~640 °C) temperatures a little propylene[33,34] is formed although its production does not increase with temperature.

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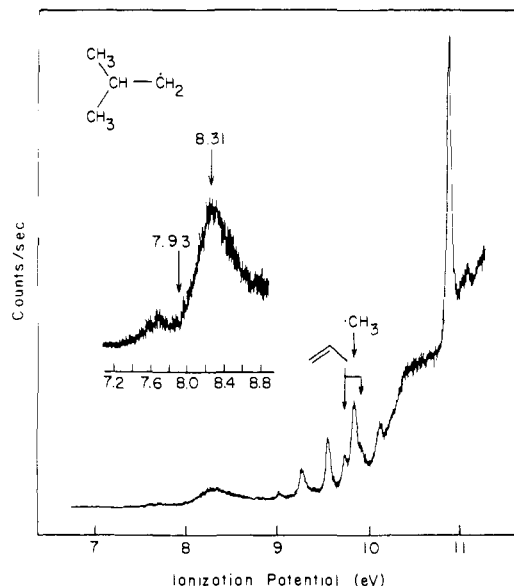
Figure 4. He I spectrum of isobutyl radical and other pyrolysis products of 3-methyl-1-butyl nitrite. Peaks in the 9.2–10-eV spectral region arise from NO, propylene, and methyl radicals. CH$_2$O is at 10.9 eV. Insert shows isobutyl radical band in greater detail. The weak band just before the isobutyl radical band is assigned to a secondary radical, possibly 2-butyl radical.

1-Butyl Radical. The Ne I spectrum of the first photoelectron band of 1-butyl radical is shown in Figure 3. At the pyrolysis temperature of 500 °C, the radical band intensity is a maximum and only small amounts of radical decomposition products are observed. The adiabatic and vertical IPs are 8.02 (+0.04 − 0.1) and 8.50 ± 0.04 eV, respectively. The adiabatic IP, chosen as the band onset, is in good agreement with a previous electron impact determination of 8.01 ± 0.05 eV.[18] No vibrational progressions could be discerned on the photoelectron band.

The very low-intensity band just before that of 1-butyl radical is in the spectral region where the first photoelectron bands of secondary alkyl radicals appear (see Table I). The low signal to noise precludes any definite assignment. The observed adiabatic and vertical IPs for this band, ∼7.3 and ∼7.6 eV, respectively, are, however, consistent with those of 2-butyl radical. The intensity of this band does not appear to increase with temperature. The 1-butyl radical precursor sample was checked for purity and found to contain no (<3%)[35] 2-butyl radical precursor (2-methyl-1-butyl nitrite). Ethylene is present in the spectrum at 500 °C and increases with temperature. At high temperatures (∼625 °C) the radical band in the 8–9-eV spectral region changes shape, having a much higher adiabatic IP coinciding closely with that of ethyl radical at 8.39 eV.[7] A very low-intensity peak at 9.7 eV, seen in He I spectra at high and low pyrolysis temperatures, may be due to small amounts of propylene.

Isobutyl Radical. The He I spectrum of the first photoelectron band of isobutyl radical is shown in Figure 4. The isobutyl radical spectrum was maximized by operating the short pyrolyzer at 685 °C (corresponding to ∼500 °C with the long pyrolyzer). The adiabatic and vertical IPs are 7.93 (+0.03 − 0.1) and 8.31 ± 0.03 eV, respectively. The adiabatic IP was chosen as the point at which there was a definite rise in the radical spectrum. The adiabatic IP is in good agreement with an electron impact IP of 8.01 ± 0.05 eV.[18] No vibrational progressions could be identified on the photoelectron band.

Again, there is a low-intensity band in the spectral region where secondary alkyl radical bands appear (see Table I), possibly partially obscuring the onset of the primary radical band. The observed adiabatic IP of this band is ∼7.30 eV. The apparent band maximum at ∼7.68 eV is mainly due to He Iβ ionization of the NO peak at 9.55 eV, and therefore the vertical IP of this

band has not been determined. The adiabatic IP observed is close to that of 2-butyl radical, considering that the onset of a very low-intensity band would be expected to yield a value that is too high. However, no definite assignment can be made. The isobutyl radical precursor sample was checked for purity and had no (<1%)[35] 2-butyl radical precursor. Over the 500–600 °C range, the ratio of the secondary radical band to the isobutyl radical band increases with temperature. Propylene, at 9.74 eV, and methyl radical, which coincides with the NO peak at 9.84 eV, are seen in Figure 4, and their production increases with temperature.

Neopentyl Radical. In Figure 5 is shown the He I spectrum of the first photoelectron band of neopentyl radical. A low pyrolysis temperature, 600 °C with the short pyrolyzer, was necessary to maximize the neopentyl radical spectrum. The adiabatic and vertical IPs are 7.88 ± 0.05 and 8.25 ± 0.03 eV, respectively. The adiabatic IP, chosen as the band onset, is in good agreement with an electron impact IP of 7.91 eV.[29] No vibrational structure could be resolved on the band.

The photoelectron band that appears at lower ionization potentials is in the tertiary alkyl radical spectral region. The observed adiabatic and vertical IPs for this band are ∼6.75 and ∼6.98 eV, respectively, from the spectra taken at temperatures where the neopentyl radical band is a maximum. From a spectrum taken 50 °C higher, to maximize the tertiary radical band, a slowly rising onset at 6.68 eV was observed for this band. No definite spectral assignment can be made. The IPs are fairly close to those of *tert*-butyl radical (see Table I) and higher than would be expected for the tertiary C$_5$, 2-methyl-2-butyl, radical. By electron impact, the IP of 2-methyl-2-butyl radical is 0.08 eV lower than that of *tert*-butyl radical.[29] Preliminary results indicate that the photoelectron spectrum of this radical, made directly from its nitrite precursor, has a slowly rising onset at ∼6.65 eV.[36] No (<5%)[35] 2-methyl-2-butyl radical precursor was found in the neopentyl radical precursor sample. Over the 600–740 °C range, with the short pyrolyzer, the intensity of this tertiary radical band increases with temperature, relative to the neopentyl radical band. The spectrum of isobutylene, a series of three peaks, the first and third of which are approximately coincident with the NO peaks at 9.26 and 9.55 eV,[34,37] and the spectrum of methyl radical are observed in Figure 5. These pyrolysis products increase with temperature.
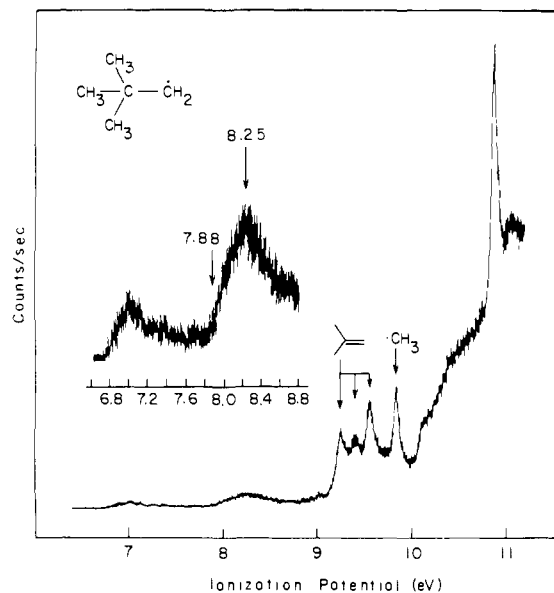

Figure 5. He I spectrum of neopentyl radical and other pyrolysis products of 3,3-dimethyl-1-butyl nitrite. Peaks in the 9.2–10-eV spectral region arise from NO, isobutylene, and methyl radical. CH$_2$O is at 10.9 eV. Insert shows the neopentyl radical band in greater detail. The band at 7 eV is assigned to a tertiary radical, possibly 2-methyl-2-butyl radical.

(35) Analyzed by NMR (500 MHz, Southern California Regional NMR Facility).

(36) Kruppa, G. H.; Beauchamp, J. L., unpublished results.
(37) A photoelectron spectrum of an authentic sample was taken on our instrument to obtain the shape of the spectrum.

Table II. Thermochemical Data for Radicals and Data for Cations Derived from Adiabatic Ionization Potentials Determined by Photoelectron Spectroscopy[a]

R	$\Delta H_f(R\cdot)$	$\Delta H_f(R^+)$[b]	D(R–H)	D(R$^+$–H$^-$)[b]	PA(alkene)[b,c]	alkene
CH_3	35.1[d] (35.1)[e]	262.0 (262.0)[e]	105.1	314.6		
CH_3CH_2	28.3[f] (25.9)	221.8 (219.4)	100.6	276.7	156.4	C_2H_4
2-C_3H_7	20.0[f] (18.2)	189.7 (187.9)	96.9	249.2	180.9	C_3H_6
t-C_4H_9	10.3[f] (8.7)	164.8 (163.2)	94.8	231.9	196.6	i-C_4H_{10}
1-C_3H_7	22.6[g] (21.0)	210.5 (208.9)	99.5	270.0	160.1	C_3H_6
i-C_4H_9	15.0[h] (13.4)[h]	197.9 (196.3)	99.5	265.0	163.5	i-C_4H_{10}
neo-C_5H_{11}	7.1[h,i] (8.7)	188.8 (190.4)	99.5	263.8		
1-C_4H_9	17.0[h] (15.4)[h]	201.9 (200.3)	99.5	267.0	163.6	1-C_4H_{10}
2-C_4H_9	13.8[j] (13.0)	181.0 (180.2)	96.3	246.1	181.7	2-C_4H_{10}

[a] All quantities in kcal/mol at 298 K. Alkane and alkene heats of formation and the ΔH_f(H) from ref 46. Error limits ±0.5 kcal/mol for methyl, ±1.1 kcal/mol for ethyl, 2-propyl, 1-propyl, and 2-butyl, ±1.2 kcal/mol for *tert*-butyl, ±2.3 kcal/mol for neopentyl, and ±3 kcal/mol for 1-butyl and isobutyl. [b] All ionic heats of formation are calculated by using the convention that the heat of formation of an electron at rest is zero at all temperatures. Therefore, $\Delta H_f(H^+)$ = 365.7 and $\Delta H_f(H^-)$ = 34.7 kcal/mol, ref 5b. [c] The proton affinity calculated is to form the given cation. This may not refer to protonation at the most probable site in the alkene. [d] Reference 42. [e] Quantities in parenthesis are the radical heats of formation from ref 42 and the corresponding cation heats of formation derived from the photoelectron data. [f] Designated "1981 values", ref 41. [g] Reference 43. [h] Calculated assuming D(R–H) $\simeq$ D(1-C_3H_7–H) $\pm$ 2 kcal/mol. [i] Essentially the same value for ΔH_f(neo-C_5H_{11}) is obtained from an experimental determination of D(neo-C_5H_{11}–H) = 99.3 ± 1 kcal/mol, ref 47a. This is in reasonable agreement with a 4.0 ± 1 kcal/mol difference between D(R–H) for methane and neopentane, ref 47b.
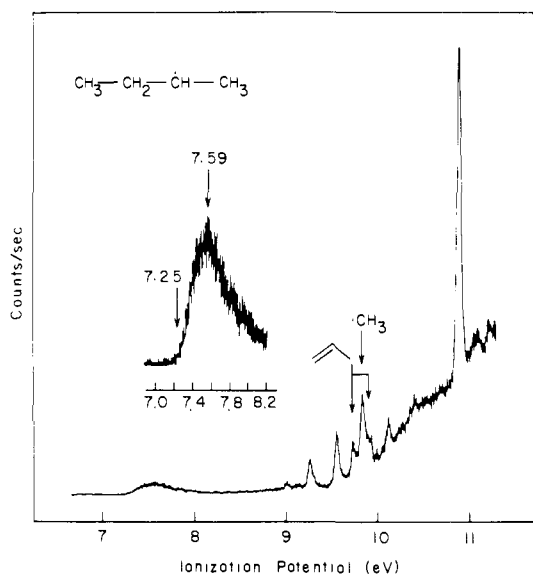

Figure 6. He I spectrum of 2-butyl radical and other pyrolysis products of 2-methyl-1-butyl nitrite. Peaks in the 9.2–10-eV spectral region arise from NO, propylene, and methyl radical. CH_2O is at 10.9 eV. Insert shows the 2-butyl radical band in greater detail.

2-Butyl Radical. The He I spectrum of the first photoelectron band of 2-butyl radical is shown in Figure 6. No vibrational structure was observed on the band. Therefore, the band onset, at 7.25 ± 0.02 eV, was chosen as the adiabatic IP. The vertical IP is 7.59 ± 0.03 eV. An electron impact IP of 7.41 ± 0.05 eV[18] is approximately an average of the adiabatic and vertical IPs determined in this work. The same situation is true for another secondary radical, 2-propyl radical, where the electron impact IP coincides approximately with the average of the adiabatic and vertical IPs determined by photoelectron spectroscopy.[7] In both of these cases the onset of the radical photoelectron spectrum is quite sharp and there is no evidence of hot bands.

The spectra of propylene and methyl radical are seen in Figure 6 and increase with temperature. A very small amount of 2-butene is observed at both low and high pyrolysis temperatures.

Discussion

Thermochemistry. Table II summarizes thermochemical data relating to the radicals and quantities derived for the ions from the photoelectron spectra of the radicals studied in this work. Similar data from earlier studies of other alkyl radicals are also included.

The calculation of an accurate ionic heat of formation requires an adiabatic ionization potential for the radical and an accurate

radical heat of formation. An adiabatic IP corresponds to formation of the ion in its ground vibrational state at the (local) minimum corresponding most closely to the neutral structure. If the radical and cation have similar equilibrium structures, the first peak in an observed vibrational progression on the photoelectron band, or alternatively the band onset of a featureless band, can be confidently assigned to the adiabatic IP. However, if a large change in the equilibrium geometry occurs upon ionization, the adiabatic ionization process may not be observed. The photoelectron spectrum of HCO radical[38] provides an example of the latter case. Ionization of nonlinear HCO (HCO angle of 123°) forms HCO$^+$, which has a linear equilibrium geometry. From a Franck–Condon analysis of the first photoelectron band, Dyke and co-workers concluded that the adiabatic IP of HCO is 0.28 eV lower than the first peak in the observed vibrational envelope.

As discussed in the introduction, the cations corresponding to the primary radicals studied in this work may not be at local minima, and thus there may be no true adiabatic IPs corresponding to their formation. Instead, the true adiabatic IP would correspond to formation of the rearrangement product and may not be experimentally observable due to low Franck–Condon factors. Nevertheless, the photoelectron spectra could be used to calculate useful thermochemical quantities because the observed photoionization processes are indeed limited by the accessible Franck–Condon region.

To calculate the heat of formation of the cation with a structure *closest* to that of the radical, the vertical ionization potential would be used. Even in those cases where the corresponding cation is at a potential energy minimum, the equilibrium cation geometry is somewhat different from the radical geometry. This is reflected in the photoelectron spectra of alkyl radicals, such as 2-propyl and *tert*-butyl radicals, since adiabatic and vertical IPs do not coincide.[7] To calculate heats of formation of the primary cations in a manner consistent with those calculated for known stable cations by allowing them to reflect stabilization achieved by the cation by small deviations from the radical geometry, the lowest energy ionization observed in the radical photoelectron spectrum has been used. If the cation is at a local minimum, this quantity should be the true adiabatic IP. In the absence of a local minimum corresponding to the cation, it represents a somewhat vague limit. With these qualifications in mind, the apparent adiabatic IP of 1-propyl radical, for example, is associated with formation of 1-propyl cation. It is noted that the heat of formation of 1-$C_3H_7^+$ in Table II is much higher than that of 2-$C_3H_7^+$ calculated using the adiabatic IP of 2-propyl radical. In addition, and of particular importance for the discussion below, the apparent adiabatic ionization potential of the previously studied ethyl radical cor-

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responds more closely to formation of a primary cation than the stable bridged structure.[7]

The other quantity needed to calculate an accurate cation heat of formation from the photoelectron data is a heat of formation for the radical. Recently, the accuracy of the widely accepted Benson values[39] for the heats of formation of alkyl radicals, other than methyl radical, has been questioned. Many experiments by other workers have suggested that the heats of formation should be revised upward.[40,41] The most recent review on the subject,[42] however, after examining the conflicting evidence concerning the heat of formation of *tert*-butyl radical, which is at the center of the controversy, adopted a slightly updated version of the previously well-accepted lower values for alkyl radical heats of formation.

In this work, the somewhat higher radical heats of formation are used. Employing the heats of formation of 1-propyl[43] and 2-butyl[44] radicals from recent determinations and the heats of formation of 1-butyl, isobutyl, and neopentyl radicals, calculated assuming $D(R-H)$ is approximately equal to $D(1-C_3H_7-H)$, the heats of formation of the corresponding ions were calculated. Thermochemical data derived from photoelectron data[7] on other alkyl radicals were calculated also using recently determined values for the radical heats of formation (the designated "1981 values" of Doering[41,45]). The thermochemistry of the methyl, ethyl, 2-propyl, and *tert*-butyl cations listed in Table II is somewhat different from previously cited[7] values determined from the photoelectron spectra of the radicals, because slightly higher radical heats of formation have been used.

For comparison, the previously well-accepted lower radical heats of formation and the resulting cation heats of formation derived from the photoelectron data are listed in parentheses in Table II. These values will not be used in subsequent discussion. However, it is noted that the relative cation heats of formation differ only slightly between the two sets. Since the large majority of the comparisons between the photoelectron data and other experimental or theoretical studies involve relative cation heats of formation, not absolute values, the conclusions are nearly independent of the set of radical heats of formation used.

Combining the heats of formation of the ion with known alkane and alkene heats of formation, the hydride affinity of the ion ($D(R^+-H^-)$) and the proton affinity (PA) of the corresponding alkene can be determined and are listed in Table II. It has been noted that typical primary, secondary and tertiary ions have characteristic hydride affinities and that the hydride affinities can be used to evaluate the relative stabilities of ions.[29,48] Referring to the data in Table II, all the primary ions have similar hydride affinities. Furthermore, β- and, to a lesser extent, γ-methyl substitution in a primary ion decreases the hydride affinity, indicating an increased stability of the ion. Similarly, 2-butyl cation has a hydride affinity somewhat below that of 2-propyl cation.

Thresholds for formation of fragment ions from hydrocarbons often correspond to formation of the most stable isomer, even when extensive rearrangements are required.[49] Exceptions are known, however. For example, photoionization appearance potentials at 300 K for CH_3 ($\Delta H_{f\,298}(CH_3) = 35.1$ kcal/mol[39]) loss from *n*-pentane and isopentane[50] give $\Delta H_{f\,298}(C_4H_9^+) = 182.3 \pm 1.0$ and 181.0 ± 1.0 kcal/mol, respectively, both of which apparently correspond to 2-$C_4H_9^+$ and not to *tert*-$C_4H_9^+$. These values are in very close agreement with the $\Delta H_{f\,298}(2$-$C_4H_9^+)$ of 181.0 ± 1.1 kcal/mol determined here. The ionic heats of formation derived above were calculated assuming the appearance potential (AP) measured at 298 K is the energy to form the products of the fragmentation process at 298 K from reactants at 298 K. A recent photoionization study[51] assumed that the AP measured at 298 K corresponds to products formed at threshold with 0 K translational energy and essentially 0 K internal energy from reactants at 298 K. On the basis of this assumption, a slightly higher heat of formation at 298 K for 2-butyl cation of 184.3 ± 0.7 kcal/mol was calculated by using AP measurements of $C_4H_9^+$ from 2-substituted butanes.[52] The 3.3 ± 1.4 kcal/mol discrepancy between the photoelectron and these photoionization results may be due to an adiabatic AP that is too low in intensity to observe, an adiabatic IP that was chosen too low, or a radical heat of formation that is too low. Ideally the adiabatic IP is chosen as the maximum of the first peak in a resolved vibrational progression, and this should correspond approximately to the Q band of the $0,0 \leftarrow 0,0$ transition energy.[7] For the 2-propyl and *tert*-butyl radical photoelectron spectra, the adiabatic ionization potentials, which were chosen as the maximum of the first vibrational peak, are approximately 0.03–0.04 eV higher than the band onset. By comparison, we would expect that the adiabatic IP for 2-butyl radical, which was chosen as the band onset, could be too low by no more than 1 kcal/mol. Since the pyrolysis temperature is low and the band onset is sharp, it seems unlikely that hot bands contribute to the spectrum.

From equilibrium constants for proton-transfer reactions measured in the high-pressure ion source of a mass spectrometer, the heat of formation of 2-$C_4H_9^+$ is calculated to be 183.2 ± 2.2 kcal/mol, relative to a heat of formation for 2-$C_3H_7^+$ of 191.7 ± 2.1 kcal/mol (a difference of 8.5 kcal/mol).[53] From rate constants of proton-transfer reactions observed in a pulsed ion cyclotron resonance spectrometer, the heat of formation of 2-$C_4H_9^+$, relative to that of t-$C_4H_9^+$, was found to be $+14.6 \pm 1.4$ kcal/mol.[54] From the photoelectron results presented in Table II, the heat of formation of 2-$C_4H_9^+$ relative to 2-$C_3H_7^+$ is -8.7 ± 1.6 kcal/mol and relative to t-$C_4H_9^+$ is $+12.0 \pm 1.7$ kcal/mol, in good agreement with the proton-transfer results.

Solution-phase data on the relative heats of formation of cations can be compared to the gas-phase results. The difference between the heats of formation of 2-butyl and *tert*-butyl cations, in a SO_2ClF/SbF_5 solution, has been measured by calorimetry to be 14.3 ± 0.5 kcal/mol.[4b] Our gas-phase determination of this energy difference is 16.2 ± 1.6 kcal/mol. These agree within the uncertainties in the measurements, supporting previous conclusions that differential solvation energetics of isomeric cations are small.[2a,4b,55]

The difference between the heats of formation of 1-propyl and 2-propyl cations is 20.8 ± 1.6 kcal/mol as determined from the photoelectron data. This is somewhat larger than a previous value of 16 kcal/mol calculated from IPs for the radicals determined by electron impact.[18] The third $C_3H_7^+$ isomer, protonated cyclopropane, is probably intermediate between the two, but its heat

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(45) Doering's evaluation (ref 41) of the recent determinations of radical heats of formation is not a critical one. The designated "1981 values" are averages of the most recent values available at that time. However, in all cases but that of *tert*-butyl radical, the values averaged by Doering are quite close to each other, and very few new determinations have appeared since then. The average value for the heat of formation of *tert*-butyl radical chosen by Doering, 10.3 kcal/mol, was recently supported by remarks made at the 1983 ACS Conference in Seattle, WA. S. W. Benson reported that a study of isobutane bromination yields a value of 10.2 ± 0.5 kcal/mol and R. Walsh, M. J. Rossi, and D. M. Golden reported that a reexamination of iodine kinetics yields a lower limit of 9.7 kcal/mol for this quantity.

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of formation is not well-known.[56] This difference of 20.8 kcal/mol can be compared to a recent estimate of 16.4 ± 0.4 kcal/mol for the energy of activation for proton exchange in 2-propyl cation in SO$_2$ClF/SbF$_5$ solution.[19,57] This was derived from NMR line-shape analysis over the 0–40 °C temperature range. One mechanism proposed for the exchange involves isomerization of 2-propyl to 1-propyl cation followed by closure to a protonated cyclopropane (which is necessary to account for ^{13}C scrambling). Formation of 1-propyl cation is likely to be the most endothermic step. Therefore, the 16.4 kcal/mol activation energy can be taken to be a measure of the difference in energy of the two isomers in solution plus the activation energy for the reverse reaction, assumed to be very small in the case of a primary to secondary cation rearrangement.[57] If this mechanism is correct, then it would appear that solvent participation in the isomerization must be important. Another explanation is that the primary cation is not an intermediate. The other mechanism proposed[57] involves a concerted rearrangement involving only 2-propyl cation and protonated cyclopropane. The activation energy may then reflect the energy difference between these two structures.

The NMR spectrum of 2-butyl cation[22] indicates that scrambling of all the protons occurs over the –110 to –40 °C temperature range, compared to 0–40 °C for 2-propyl cation.[57] Since the barrier for this process must be much lower than for the equivalent process in 2-propyl cation, a primary cation intermediate was considered to be unlikely. This conclusion is confirmed by our results since the differences between 1- and 2-propyl cation and 1- and 2-butyl cation are both ∼20 kcal/mol. Assuming a protonated methylcyclopropane intermediate, Saunders et al.[22] calculated an E_a of 7.5 ± 0.1 kcal/mol for complete proton scrambling in 2-butyl cation. At higher temperatures, 2-butyl cation converts to *tert*-butyl cation. From the rate observed at –41 °C and assuming a normal log A, the barrier to this reaction is estimated to be 18 kcal/mol.[22] Isobutyl cation was suggested as a possible high-energy transition state for the reaction so that 18 kcal/mol could represent the energy difference between 2-butyl and isobutyl cations. An alternative mechanism proposed involves cyclization of 2-butyl cation to a protonated methylcyclopropane and then a concerted rearrangement through a high-energy transition state to give *tert*-butyl cation without an isobutyl cation intermediate. The gas-phase energy difference between 2-butyl and isobutyl cation isomers, 16.9 ± 3 kcal/mol from the photoelectron results, is consistent with the intermediacy of isobutyl cation.

A closer examination of these comparisons may be used to support an expected, albeit weak, trend in solvation energetics. The gas-phase difference in the heats of formation of 2-butyl and *tert*-butyl cations is 1.9 kcal/mol larger than the solution-phase value. Assuming 1-propyl cation is an intermediate in the rearrangement of 2-propyl cation, the gas-phase difference in their heats of formation is 4.4 kcal/mol larger than the value in solution. Disregarding the comparison with the energetics for rearrangement of 2-butyl to *tert*-butyl cation in solution, which is only an approximate value, the two differences listed above suggest that solvation energies decrease in the order primary ion > secondary ion > tertiary ion. This trend can be explained by the Born model of ionic solvation. In a tertiary ion the charge is expected to be more delocalized, extending over a larger volume than in a primary ion, and thus the tertiary ion is more poorly solvated.

Radical and Cation Structures. The first photoelectron bands of the primary and secondary alkyl radicals studied in this work are fairly broad and, with the exception of 1-propyl radical, exhibit no resolved vibrational structure. This is indicative of significant geometry change on ionization, which has been found for other acyclic alkyl radicals larger than methyl radical.[7]

ESR and IR spectroscopy and theoretical calculations of the radicals yield a fairly detailed picture of the radical structures. Matrix isolation studies of infrared spectra[58–60] of primary and
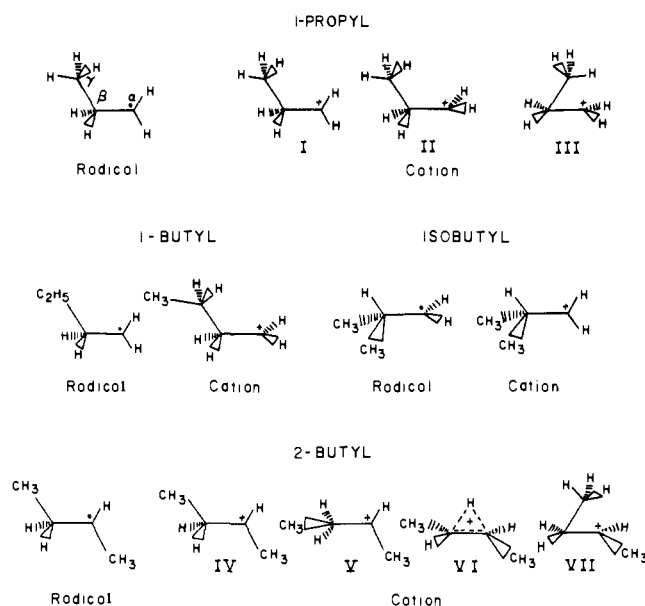

Figure 7. Preferred radical conformations inferred from ESR spectra and cation conformations taken from theoretical calculations.

secondary radicals have shown that CH stretching frequencies associated with the radical centers are typical of centers having sp^2 hybridization. From this it is inferred that primary and secondary radical centers are nearly planar. Geometry-optimized ab initio calculations give out-of-plane angles of 9–11° for 1-propyl,[61] isobutyl, and neopentyl radicals.[62] Effects of the unpaired electron on bonds β to the radical center have been observed. Infrared spectroscopy indicates that the β C–H bonds in alkyl radicals are long and weakened compared to alkane C–H bonds.[58] This is consistent with the lengthening of bonds β and eclipsed to the radical center observed in theoretical calculations.[61,62] These calculations also indicate that the C$_\alpha$–C$_\beta$ bond is somewhat shorter than a normal C–C single-bond length.

ESR spectra of radicals have been interpreted in terms of preferred radical conformations and barriers to rotation about the C$_\alpha$–C$_\beta$ bond. Results of analyzing many alkyl radical ESR spectra suggest that the equilibrium conformations in alkyl radicals are determined by a delicate balance between steric repulsions and the optimization of β C–H hyperconjugation with the singly occupied p orbital on the radical center.[63] The conformational preferences appear to be weak, however.[63] For example, the rotational barriers about the C$_\alpha$–C$_\beta$ bond in 1-propyl and isobutyl radicals estimated from their ESR spectra are very low (≤0.5 kcal/mol).[63,65,69] Theory is in agreement with this picture.[61,62]

The structure of 1-propyl radical has been the most extensively studied by both theory and experiments.[58,59,61,63–69] It has been deduced from ESR data that the preferred conformation of the radical in solution has one of the C$_\alpha$–H bonds eclipsing the C$_\beta$–C$_\gamma$ bond (see Figure 7).[63–65] Two studies[66,67] at 4 K in solid argon matrices have suggested, however, that the H$_\alpha$–C–H$_\alpha$ plane actually oscillates between two minima located 10°[66b] or 30°[67] on either side of the C$_\beta$–C$_\gamma$ bond. Theoretical calculations indicate both possibilities to be very close in energy.[61,68]

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The preferred conformations of the other radicals are also shown in Figure 7. The ESR spectrum of 1-butyl radical in solution indicates that the preferred conformation of the radical is analogous to that of 1-propyl radical. One of the C_α–H bonds is eclipsing the C_β–C_γ bond.[69-71] Similarly, studies of 1-butyl radical in argon matrices have suggested that the H_α–C–H_α plane oscillates between two minima located 23°[66b] or 30°[67] on either side of the C_β–C_γ bond. Both theory[62] and the ESR spectrum of isobutyl radical in solution[63-65,69] indicate that this radical prefers to have the p orbital on the radical center eclipse the C_β–H bond. According to the ESR spectrum, the equilibrium conformation of 2-butyl radical in solution is unsymmetrical, analogous to that for 1-propyl radical in solution.[64,69,72] Presumably, the methyl groups on the α and β carbons are anti.[72] The ESR spectrum of neopentyl radical has been obtained under various conditions.[64,73-76] In one case;[74] the spectrum was used to infer that the preferred conformation has one C_β–C_γ bond eclipsed with the radical site, which is in agreement with the theoretical results.[62] The conformational preference would be expected to be very weak since the totally symmetric 6-fold rotation about the C_α–C_β bond should lead to a very small rotational barrier.[76,77] Indeed, the theoretical calculations[62] yield a rotational barrier of only 160 cal/mol.

The only information available on the structures of primary ions comes from theory. The $C_3H_7^+$ potential energy surface has been the most well studied by ab initio[8,9,78,79] and semiempirical methods.[9,10] Under the constraint of maintaining C_s symmetry, three local minima were found for 1-propyl cation by using ab initio techniques and an STO-3G basis set.[78] Although higher level calculations[8,79] reveal that these geometries are not local minima, their energies and structures provide useful information about the $C_3H_7^+$ potential energy surface in the region of the radical structure. As shown in Figure 7, these three local minima correspond to a conformation very similar to that of the radical (I), a conformation similar to the first except that the C_α–H bonds are staggered with respect to the C_β–C_γ bond (II), and a structure resembling that of a distorted corner-protonated cyclopropane (III). The cation centers are planar or nearly so. For example, structure II has an out-of-plane angle of 5° with the hydrogens bent toward the terminal methyl group. All three geometries have C_α–C_β bonds that are shorter than C–C bonds in propane. In structures II and III, where the empty p orbital is eclipsing the C_β–C_γ bond, the C_α–C_β bond is shorter than the C_α–C_β bond length calculated for 1-propyl radical.[61] This preference for optimizing the interaction between the empty p orbital and the C_β–C_γ bond is also reflected in the relative energies of these structures. The most detailed calculation of their energies, including polarization functions at the 6-31G* level, determined that structure III is more stable than I by 4.7 kcal/mol and I is 1.8 kcal/mol higher in energy than II.[79] Another calculation, which included electron correlation effects, also found that I is higher in energy than II, in this case by 2.0 kcal/mol.[9] This energy difference is assigned to the rotational barrier about the C_α–C_β bond in II.[78,79] Thus, in the absence of symmetry constraints, I is not at a local minimum. On the basis of the relative energies of various $C_3H_7^+$ structures calculated at the 6-31G* level, it is concluded that III can be considered as a distortion of corner-protonated cyclopropane and not a local minimum. Geometry optimization at the 6-31G* level reveals that 1-propyl cation II is not a local minimum on the potential energy surface.[8] MINDO/3 semiempirical calculations are in agreement with these

results.[9,10] Both methods found that 1-propyl cation is converted without activation to protonated cyclopropane.[8,10] An energy for 1-propyl cation was obtained at the 6-31G* level by imposing a symmetry constraint, a C_s plane, and calculating the energy of the optimized structure I. Including electron correlation effects, 1-propyl cation I is 19.7 kcal/mol less stable than 2-propyl cation.[8] MINDO/3 calculations yield values of 18.6[10] and 18.87[9] kcal/mol for the energy difference between 1-propyl and 2-propyl cations. These theoretical values are in good agreement with the experimental difference in energy between 1-propyl and 2-propyl cations, 20.8 ± 1.6 kcal/mol, determined from the photoelectron data. The ab initio value is in closest agreement, although it would have been expected that this value be somewhat larger than the experimental since II is predicted to be the more stable 1-propyl structure. Given the essentially free rotation about the C_α–C_β bond in the radical, the adiabatic IP of 1-propyl radical should most closely correspond to formation of 1-propyl cation II.

Although detailed theoretical studies of the $C_4H_9^+$ and $C_5H_{11}^+$ potential energy surfaces are not available, ab initio techniques have been used to determine the most stable conformations of the radical-like, or classical, structures of the cations. Using a set of fixed standard geometries appropriate for classical carbonium ions and a STO-3G basis set, the energy of the eclipsed and perpendicular conformations (I and II, respectively, for 1-propyl cation) of 1-propyl, 1-butyl, isobutyl, neopentyl, and 2-butyl cations have been calculated.[80] The results indicate that the preferred conformation of the cation is determined largely by the relative hyperconjugative abilities of the bonds at the β carbon. C–C hyperconjugation is found to be much more effective than C–H hyperconjugation. This is in contrast to the weak preference for C–H hyperconjugation displayed by the radicals. The stronger conformation preferences displayed by primary cations compared to primary radicals has been noted previously.[81] The preferred conformations are shown in Figure 7. 1-Propyl cation prefers the perpendicular (II) over the eclipsed conformation by 2.5 kcal/mol at this level of calculation. Similarly, 1-butyl cation prefers the perpendicular conformation by 3.7 kcal/mol. To maximize C–C hyperconjugation, isobutyl cation prefers the eclipsed conformation by 2.7 kcal/mol. For neopentyl cation, neither conformation is preferred and so there is no barrier to rotation about the C_α–C_β bond, which is to be expected by symmetry. The perpendicular conformation of 2-butyl cation (V) is preferred over the eclipsed conformation (IV) by 2.2 kcal/mol.

The relative energies of the classical $C_4H_9^+$ species were also determined at the STO-3G level. 1-Butyl, isobutyl, and 2-butyl cations are 37, 37, and 17 kcal/mol, respectively, higher than *tert*-butyl cation according to these calculations.[80] This is in reasonable agreement with the corresponding values of 37.1, 33.1, and 16.2 kcal/mol determined from the photoelectron data in Table II. The good agreement between the relative energies calculated for the classical structures of the $C_3H_7^+$ and $C_4H_9^+$ ions and the energies determined from the photoelectron data is consistent with the notion that the apparent adiabatic IPs of the radicals studied in this work correspond to formation of cations with structures similar to those of the radicals.

Even when the same bonding configuration is retained, the theoretical and experimental studies discussed above indicate that in going from the radical to the cation the preferred bond lengths, bond angles, and rotational conformations change. These geometry changes explain why the vertical and adiabatic IPs of the radicals do not coincide and should also offer possible explanations for the origin of the 540 ± 160 cm^{-1} vibration progression resolved on the 1-propyl radical photoelectron band. Those variations that correspond most closely to the change in equilibrium geometry occurring upon ionization will be most strongly excited. Since, in going from the radical to the cation, the configuration at C_α is expected to become more planar and the C_α–C_β bond is expected

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to shorten to enhance C–C hyperconjugation with the cation center, it is likely that out-of-plane bending and skeletal stretching modes are excited. Both *tert*-butyl and 2-propyl radicals undergo excitation of analogous vibrations on ionization, as evidenced from assigned resolved vibrational progressions on their photoelectron bands.[7] The corresponding frequencies for these modes in 1-propyl cation would both be approximately 1000 cm^{-1}, too high in energy to correspond to the 540-cm^{-1} mode observed and hence are probably not resolved. Another major difference between the radical and ion structures is the conformational preference of the CH$_2$ group. Thus, excitation of torsions about the C$_\alpha$–C$_\beta$ bond would be expected, but would probably involve a frequency much lower than 540 cm^{-1}. Finally, it is possible that the Franck–Condon region includes part of the reaction coordinates leading to isomerization of 1-propyl cation to 2-propyl cation (1,2-hydride shift) or a protonated cyclopropane (C–C–C bending motion). Excitation of modes leading to motion along the reaction coordinate might be observed.

The fact that the photoelectron spectra of the other primary radicals presented here do not have resolved vibrational structure is not very surprising. The vibrational structure on the photoelectron band of 1-propyl radical is weak and, with larger radicals, more torsional and vibrational modes may be excited upon ionization. The overlapping of several vibrational progressions can result in a featureless band. Although the spectrum of 2-propyl radical clearly reveals vibrational structure, the larger 2-butyl radical may also have a featureless band due to more vibrational modes being excited upon ionization. This is particularly likely given the stronger interaction of the cation center with the added β methyl than with the β hydrogens, which was indicated by the theoretical calculations. The absence of structure may also be an indication that the ion is not stable with respect to isomerization. This would result in excitation of very closely spaced vibrational levels, which in turn would tend to mask structure that would otherwise be observable. Therefore, the presence of structure on the 1-propyl radical spectrum suggests that 1-propyl cation may be at a local minimum on the C$_3$H$_7$$^+$ potential energy surface. If 1-propyl cation is formed in an energy minimum, the failure to observe unrearranged 1-propyl cation experimentally in the gas phase[1a,b,11,14,15] implies there is a low barrier to isomerization.

The general shape of the first photoelectron band also contains information regarding the ionic potential energy surface relative to the ground-state radical potential energy surface. The view of the ionic potential energy surface reflected in the photoelectron band is expected to be limited, by the Franck–Condon factors, to the region of the cation species with a geometry not very different from that of the radical. Assuming the band shape reflects the overlap of vibrational wave functions of the classical cation with those of the radical, a simple interpretation can be made. Radom, Pople, and Schleyer[80] concluded that the preferred classical cation geometry is that which maximizes C$_\beta$–C$_\gamma$ hyperconjugation with the empty p orbital on the ion center. The inductive and hyperconjugative contributions to the β-methyl stabilizing effect on alkyl cations were studied by assuming the former is conformationally independent and the latter conformationally dependent.[77] By considering structurally independent and dependent effects, the photoelectron spectra of the corresponding radicals can offer an experimental verification of these contributions.

Both vertical and adiabatic IPs of alkyl radicals generally decrease with increased substitution at the β carbon. The vertical IP is determined by that vibrational wave function in the ion that has the largest amplitude at the equilibrium geometry of the radical. Trends in vertical IPs should reflect trends in the inductive stabilization offered by the substituents since to optimize the hyperconjugation stabilization available, the cation must adopt a geometry different from that of the radical, in particular a shorter C$_\alpha$–C$_\beta$ bond. Reflecting the increasing inductive stabilization with β-methyl substitution, the vertical IPs in the series ethyl, 1-propyl, isobutyl, and neopentyl radicals are 8.51, 8.43, 8.31, and 8.25 eV, respectively, and in the series 2-propyl and 2-butyl radicals are 7.69 and 7.59 eV, respectively. The vertical

IP of 1-butyl radical (8.50 eV) is higher than that of 1-propyl radical (8.43 eV). There is no obvious explanation for this since the terminal methyl group in 1-butyl cation would not be expected to destabilize the radical-like conformation.

The difference between the adiabatic and vertical IPs is that amount of extra stabilization available when the ion is allowed small conformational deviations from the radical equilibrium geometry and thus should reflect the hyperconjugative stabilization available. This difference is 0.12, 0.28, 0.38, and 0.37 eV for the series ethyl, 1-propyl, isobutyl, and neopentyl radicals, respectively. The first two methyl substituents on the β carbon result in successive "broadening" of the photoelectron band. The last methyl group appears to have no additional hyperconjugative effect since the isobutyl and neopentyl radical bands are equally "broad". This is not surprising, since hyperconjugative stabilization is expected to be a function of the dihedral angle between the empty p orbital and the C$_\beta$–C$_\gamma$ bond.[80] The maximum hyperconjugative stabilization available from each C$_\beta$–C$_\gamma$ bond in neopentyl cation is not simultaneously achieved. Steric effects may also decrease the stabilization available per methyl group. The difference between the adiabatic and vertical IPs for 1-propyl and 1-butyl radicals is 0.28 and 0.48 eV, respectively, and for 2-propyl and 2-butyl radicals is 0.33 and 0.34 eV, respectively. Steric interactions may have some effect since it is somewhat surprising that the difference between the adiabatic and vertical IPs of 2-butyl radical is essentially the same as that of 2-propyl radical.

Radom, Pople, and Schleyer[80] concluded that for primary cations the inductive and hyperconjugative effects of the alkyl group β to the cation center make approximately equal contributions on the order of several kcal/mol and that they follow the normal inductive order: *t*-C$_4$H$_9$ > 2-C$_3$H$_7$ > C$_2$H$_5$ > CH$_3$. Our results are in general agreement with these findings.

NMR spectroscopy has been used extensively to study the low-energy conformations of 2-butyl cation.[23,25,82] An empirical additive substituent effect method for estimating ^{13}C NMR shifts was applied to the 2-butyl cation spectrum.[24] It was concluded that 2-butyl cation in SbF$_5$/SO$_2$ClF solution at low temperatures (−80 to −130 °C) is best represented as equilibrating between a classical secondary cation (structures IV and V, Figure 7) and a hydrogen-bridged species (VI) of very similar energy. From the absence of line broadening in the ^{13}C NMR spectrum of 2-butyl cation in solution at −140 °C, an upper limit of 2.4 kcal/mol for $\Delta G^\ddagger$ was determined for the degenerate 1,2-hydride shift.[82] Even in the solid state at −190 °C, there is no evidence for a static 2-butyl cation.[23] Recently, Saunders and co-workers studied the effect of isotopic perturbation[83] on the NMR spectrum of 2-butyl cations. Their interpretation of the results indicates that the secondary cation structure is at a local minimum 0.4 kcal/mol above the more stable hydrogen-bridged species, with a barrier of less than 2 kcal/mol for rearrangement of the hydrogen-bridged species to the classical cation.[25]

The heat of formation of 2-butyl cation determined in this work is in close agreement with proton transfer[53,54] and several appearance potential measurements,[50] as discussed previously. This is consistent with the NMR results. Since Franck–Condon factors for ionization to a hydrogen-bridged species would be expected to be small, the adiabatic IP probably corresponds to formation of the radical-like cation structure. If there is a low barrier to rearrangement to a more stable structure, the other techniques would be expected to measure the heat of formation of this structure. A 0.4 kcal/mol difference between the photoelectron results and the others, as suggested by the NMR experiments, could not be detected. The appearance potential measurements[52] which are only in fair agreement with the photoelectron results, yield a heat of formation of 2-butyl cation that is higher, and thus the discrepancy cannot be explained by using this argument. From structures optimized at the STO-3G and the MINDO/3 level, ab initio calculations including electron correlation effects and

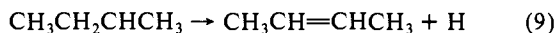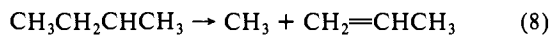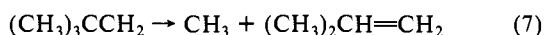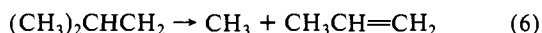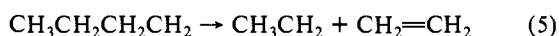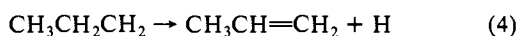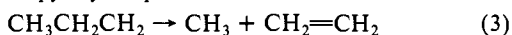(82) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 7082.
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estimating the effect of polarization functions indicate that the hydrogen-bridged 2-butyl structure (VI) is 8–10 kcal/mol lower than the classical structure.[84]   At a similar level of theory, the hydrogen-bridged structure of ethyl cation is 8 kcal/mol lower than the classical.[85]   There is evidence that the most stable ethyl cation structure is significantly different from that of ethyl radical. Heats of formation of ethyl cation determined from photoionization appearance energies, 216.0 ± 0.5[51] and 215.3 ± 1.0[86] kcal/mol, predict an adiabatic IP of ethyl radical of 8.12 ± 0.08 eV, significantly below the value of 8.39 ± 0.02 eV[7] determined by photoelectron spectroscopy and below the photoelectron band onset at $\sim$8.32 eV. The difference between the predicted and apparent adiabatic IPs suggests that hydrogen-bridged ethyl cation is 6 ± 2 kcal/mol lower in energy than the classical structure, in agreement with theory. Either the theory overestimates the stability of the hydrogen-bridged 2-butyl cation and the NMR results in stable-ion media are a better reflection of the energy differences in the gas phase, or the thermochemistry of the $C_4H_9^+$ system is not sufficiently well determined to detect the energy difference, or there is a large barrier for the rearrangement.

From fixed geometries based on optimized structures of 1-propyl and 2-propyl cations, ab initio calculations at the 4-31G level found another low-energy 2-butyl cation structure. A partially methyl-bridged structure (VII) is calculated to be 15 kcal/mol more stable than 2-butyl cation V, although a fully bridged structure, corner-protonated methylcyclopropane, is only 0.6 kcal/mol more stable than V. The NMR experiments on 2-butyl cation[22] reveal no evidence for such a stabilized structure but instead are consistent with a protonated methylcyclopropane species being 2–7 kcal/mol higher in energy than 2-butyl cation. Gas-phase experiments indicate that protonated methylcyclopropane is also higher in energy than 2-butyl cation, by $\sim$10 kcal/mol.[53] The calculations may overestimate greatly the stability of the partially methyl-bridged structure.

Thermal Decomposition of Radicals. As shown in the Experimental Section, the direct products of the thermal decomposition of the nitrite precursor are observed in the photoelectron spectra as well as other species, which can be ascribed to subsequent decomposition reactions of the initial radicals formed.[88,26] Overlapping photoelectron spectra may obscure some products and, unless a spectrum is sharp or otherwise characteristic, a positive assignment may be difficult. Only those intermediates that can survive $\sim$1 ms in the heated region will be detected in the photoionization region.
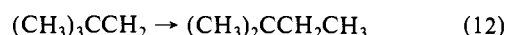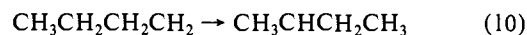
The following reactions can account for most of the products observed in the pyrolysis spectra:

$$CH_3CH_2CH_2 \rightarrow CH_3 + CH_2{=}CH_2 \qquad (3)$$

$$CH_3CH_2CH_2 \rightarrow CH_3CH{=}CH_2 + H \qquad (4)$$

$$CH_3CH_2CH_2CH_2 \rightarrow CH_3CH_2 + CH_2{=}CH_2 \qquad (5)$$

$$(CH_3)_2CHCH_2 \rightarrow CH_3 + CH_3CH{=}CH_2 \qquad (6)$$

$$(CH_3)_3CCH_2 \rightarrow CH_3 + (CH_3)_2CH{=}CH_2 \qquad (7)$$

$$CH_3CH_2CHCH_3 \rightarrow CH_3 + CH_2{=}CHCH_3 \qquad (8)$$

$$CH_3CH_2CHCH_3 \rightarrow CH_3CH{=}CHCH_3 + H \qquad (9)$$

Surface reactions may be responsible for the small amount of H atom loss products (reactions 4 and 9) since they are observed at low temperatures and their yield does not appear to increase at higher temperatures. On the basis of their Arrhenius parameters, the reaction involving C–C bond cleavage in 1-propyl radical is much faster than homogeneous H atom loss.[89]   This conclusion also applies to 2-butyl radical. Homogeneous H atom loss com-

petes so unfavorably with C–C bond cleavage that its rate has not been measured.[90]   H atom loss products for 1-butyl and isobutyl radical, 1-butene and isobutylene, respectively, could not be detected. The C–C bond cleavage reactions observed in this study ((3) and (5)–(8)) have all been reported to be the major decomposition pathways for the respective radicals.[89]

In the studies of 1-butyl and isobutyl radicals, very low-intensity photoelectron bands appeared near the onset of the photoelectron spectra assigned to these primary radicals. No positive assignment could be made due to the very low signal levels although the bands do appear in the spectral region where secondary radical photoelectron bands are located, and their apparent adiabatic and vertical IPs are not inconsistent with the spectrum of 2-butyl radical. In the neopentyl radical pyrolysis spectrum, significant amounts of a tertiary radical appeared whose spectrum is close to that of *tert*-butyl radical and could be due to the C_5 tertiary radical. An explanation consistent with these observations is the occurrence of radical isomerizations (reactions 10–12) under the conditions of our experiments.

$$CH_3CH_2CH_2CH_2 \rightarrow CH_3CHCH_2CH_3 \qquad (10)$$

$$(CH_3)_2CHCH_2 \rightarrow CH_3CHCH_2CH_3 \qquad (11)$$

$$(CH_3)_3CCH_2 \rightarrow (CH_3)_2CCH_2CH_3 \qquad (12)$$

In a study of isomeric C_4H_7 radicals by photoelectron spectroscopy,[91] several radical rearrangements are observed that have been previously noted under other experimental conditions. There is some evidence that reaction 10 has been observed before[89] by the detection of propylene, a product of 2-butyl radical decomposition, from thermolysis of 1-butyl radical.[92]   A small peak that may be assigned to propylene was observed in photoelectron spectra of the pyrolysis products of the 1-butyl radical precursor. However, reactions 11 and 12 appear never to have been observed, nor investigated, previously. Reaction 10 can be interpreted as a 1,3- or 1,2-H atom shift, both of which occur for vibrationally excited pentyl radicals with estimated activation energies of $\sim$31 and $\sim$33 kcal/mol, respectively.[93]   Similar activation energies have been measured for the β C–C bond-breaking processes, reactions 3 and 5–8. The Arrhenius A factor for the rearrangement would be expected to be significantly lower than that for a simple bond-breaking process. Reactions 11 and 12 can be explained by 1,2-CH_3 shifts. The rearrangement of neopentyl radical appears to be much more facile than that of isobutyl radical, perhaps reflecting a larger statistical factor and/or a preference for formation of a tertiary radical over a secondary radical product. Theory[94] has indicated that 1,2-CH_3 shifts, like 1,2-H shifts, are high-energy processes. It is often suggested that the lowest energy pathway for formation of such products involves elimination and readdition of the methyl group.[95]   The low-pressure conditions of our experiments make the latter route very unlikely. However, the radicals experience several collisions with the pyrolyzer wall. All three of these rearrangements could take place via heterogeneous wall-catalyzed mechanisms. Since the activation energies for the truly unimolecular rearrangement and for the decomposition may be very close, the rearrangement products would have enough energy to decompose rapidly and thus would not be detected. A heterogeneous rearrangement mechanism may offer a means by which less activated products would be formed.

Admittedly, these suggested mechanisms are somewhat speculative since no definite spectral assignments could be made except to identify the products as secondary or tertiary alkyl radicals. Hydrogen atom abstraction from the nitrite precursor by a radical could result in secondary radicals being observed in the 1-butyl

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and isobutyl radical spectra, but no tertiary radical could be produced directly by hydrogen atom abstraction from the neopentyl radical precursor. Furthermore, there is no evidence of such reactions from the many studies that used organic nitrites to cleanly produce specific radicals.[7,26,91] No alternative nitrite decomposition pathways, which would be competitive with reactions 1 and 2 and lead to radical products, can be proposed. It has been reported that 1-butyl radical eliminates molecular hydrogen, presumably to form 1-methylallyl radical.[96] Isobutyl radical undergoing an analogous reaction would form 2-methylallyl radical. These decomposition pathways cannot explain the additional radical bands observed. The adiabatic IPs of these allylic radicals are 7.49 and 7.90 eV, respectively.[90] The band onsets are ~ 0.1 eV lower but still too high to correspond to those observed for the low-intensity bands appearing near the onset of the 1-butyl and isobutyl radical photoelectron bands.

The primary benefit of these observations may be to suggest new experiments. If these reactions are unimolecular, they provide evidence, at high temperatures, for reactions previously thought not to be competitive with the decomposition reactions. If they are wall catalyzed, they draw attention to possible complications in kinetic experiments involving these radicals.

Conclusion

Photoelectron spectroscopy is unique as an experimental technique for obtaining thermochemical and structural information about high-energy carbonium ion isomers. Analysis of the photoelectron spectra of 1-propyl, 1-butyl, isobutyl, neopentyl, and 2-butyl radicals, combined with the heats of formation of the radicals, yields heats of formation of 1-propyl, 1-butyl, isobutyl, neopentyl, and 2-butyl cations. An examination of the spectra presented here and the spectra of ethyl and 2-propyl radicals reported previously[7] reveals trends in ionization potentials which

can be interpreted in terms of inductive and hyperconjugative effects of methyl substituents β to a primary or secondary cation center.

The primary cation heats of formation have been discussed in light of theoretical calculations and energetics of cation rearrangements in solution which may involve primary cations as high-energy transition states or intermediates. The heat of formation of 2-butyl cation derived here is in good agreement with values obtained from appearance potential measurements and equilibrium constants for proton-transfer reactions. This agreement suggests that if classical 2-butyl cation does easily rearrange to a more stable hydrogen-bridged structure, the difference in energy between the classical and rearranged structure is small. NMR experiments support this suggestion. Photoelectron data also yield the difference between the heats of formation of 2-butyl and *tert*-butyl cations. This value is in close agreement with that from solution calorimetric studies. This agreement and the results of comparisons made between relative heats of formation of gas-phase cations and energetics of reactions in stable-ion media support previous studies which indicate that differential solvent effects on cation isomers are small. There is some indication that solvation energies may decrease slightly in the order primary ion > secondary ion > tertiary ion.

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Excited States of Polyene Radical Cations: Limitations of Koopmans' Theorem

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Abstract: The electronic absorption spectra of the molecular cations of butadiene, hexatriene, and octatetraene in Ar matrices are presented and compared to earlier related results where possible. From these specta and the accompanying qualitative and quantitative theoretical considerations it must be concluded the Koopmans' theorem breaks down for all excited states of linear conjugated polyene molecular cations (and anions) due to pronounced mixing between Koopmans' and non-Koopmans' configurations. The implications of this breakdown for the widely applied interpretation of linear polyene ultraviolet photoelectron spectra on the basis of orbital energies are discussed.

There has been a long and rich history of experimental and theoretical investigations on the nature of linear polyene excited states.[1] For many years these were thought to be understood quite well within the framework of one-electron theories such as those

commonly employed in MO models. Indeed, the position and intensity of the first band in the electronic absorption (EA) spectra of linear polyenes was reproduced with reasonable accuracy by properly parametrized procedures. The puzzling phenomenon of the unusual Stokes shift between the first absorption and fluorescence band onsets[2] was usually explained on the basis of Franck-Condon arguments.[3]

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