STUDIES OF ALKYL FREE RADICALS AND REACTION MECHANISMS BY PHOTOELECTRON SPECTROSCOPY

Thesis by

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Finally, I would like to thank Caltech for almost five years of financial support, and IBM for a Fellowship.

This thesis is dedicated to the memory of Maude Houle, my grandmother, and Don Louis Bunker, my teacher and friend.

ABSTRACT

Application of vacuum ultraviolet photoelectron spectroscopy (UPS) to the study of simple alkyl free radicals and organic reaction mechanisms is described. A brief overview of the field of UPS of chemical transients, including a survey of the relevent literature, and a general introduction to topics covered in this thesis are given in Chapter 1. Chapters 2, 4 and 5 present results of UPS investigations of the first photoelectron bands of alkyl radicals produced by pyrolysis of the corresponding alkyl nitrites. Spectra have been obtained for methyl, ethyl, 1-propyl, 2-propyl, tert-butyl, cyclopentyl, cyclohexyl and 2-norbornyl radicals. Adiabatic ionization potentials determined for these species are used to calculate heats of formation of the ions, heterolytic bond dissociation energies of the corresponding alkanes, and proton affinities of the corresponding olefins. The shapes of the bands are discussed qualitatively in terms of structural differences between neutrals and positive ions. Chapter 3 is a discussion of the lowest energy conformations of ethyl and tert-butyl radicals. In particular, ESR and theoretical results from the literature are used to discuss the question of the planarity of alkyl radical centers. Chapters 4 and 6 present results of studies of the thermal decomposition mechanisms of 2-norbornyl, cyclopentyl and cyclohexyl radicals. Pyrolysis of the radicals is readily observed under the conditions necessary for their generation. The mechanisms deduced from the spectra are compared to those resulting from studies using classical techniques. In Chapter 7, experiments designed to assess the fate of reaction exothermicity in the pyrolysis of some strained azo compounds are described. The results indicate that very little of the available energy is released to vibration of the N_2 fragment. The implications of this observation for the transition states of the reactions that were studied are discussed.

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CHAPTER I

Introduction to the Photoelectron Spectroscopy of Transients

Since the first molecular photoelectron spectra appeared in the literature in the early 1960s, the field of photoelectron spectroscopy (PES) has undergone enormous growth.[1-3] The development of commercially available, high-resolution spectrometers has opened the field to a variety of chemists, who have applied the technique to the study of electronic properties of whole classes of molecules in hopes of gaining a better understanding of fundamental principles of structure and reactivity. There remains, however, one major area of gas-phase, vacuum ultraviolet PES that is still in the early stages of development: the study of open- and closed-shell reactive intermediates and other transient species.

The first experiments published in this area involved atoms and excited diatomics produced in a discharge.[4,5] Since then, the list has expanded to include organic and inorganic radicals and closed-shell transients, small negative ions, and van der Waals complexes of the noble gases. Techniques used for generation of these species include microwave discharge, low- and high-temperature pyrolysis, atom-molecule reactions, and expansion through a supersonic nozzle. In Tables I-IV[6] is presented a summary of work performed to date, including precursors, methods of generation, and first ionization potentials (IPs).[4,5,7-65] The lists given here are as complete as possible, except for the closed-shell inorganic molecules. Only a representative sample of these is given: the interested reader is referred to work by A. F. Orchard, J. Berkowitz and H. W. Kroto. Negative ion photodetachment spectra, obtained chiefly by W. C.

Table I. Photoelectron data for open- and closed-shell organic transient molecules.

Species	Source	IP (eV) A	IP (eV) V	Vibrational Structure (cm^{-1})	Reference
Open Shell					
$:CF_2$	MWD^a C_2F_4	11.42^{b,c}	12.24	650	7
$CHO\cdot$	CH + O in flame	--	~8.2	--	8
$CH_3\cdot$	Pyrolysis	9.82	9.82	720, 2720	9
	$CH_3N{=}N{-}CH_3$	9.84^c	9.84	1380	10, 11
$CD_3\cdot$	Pyrolysis	9.83^c	9.83	1050	10
	$CD_3N{=}N{-}CD_3$				
$CH_3\dot{C}H_2$	Pyrolysis	8.39	8.51	--	11
	$CH_3CH_2CH_2ONO$				
$CH_3\dot{C}D_2$	Pyrolysis	8.38	8.50	--	11
	$CH_3CD_2CH_2ONO$				
$CH_3CH_2\dot{C}H_2$	Pyrolysis	8.16	8.47	500	12
	$CH_3CH_2CH_2CH_2ONO$				
$CH_3\dot{C}HCH_3$	Pyrolysis	7.36	7.69	730, 970	11
	$(CH_3)_2CHCH_2ONO$				

Table I (continued)

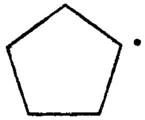
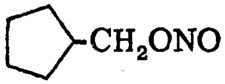
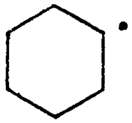
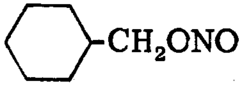
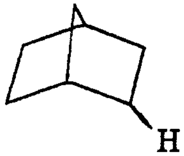
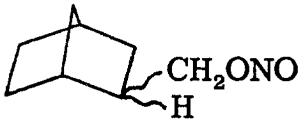
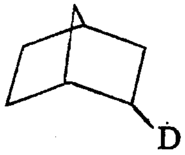
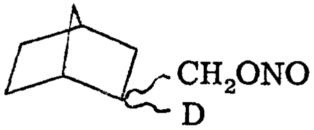
Species	Source	IP (eV)		Vibrational Structure (cm^{-1})	Reference
		A	V		
$\cdot C(CH_3)_3$	Pyrolysis	--	6.95	410, 800	9
	t-bu-N_2-t-bu	6.58[b, c]	6.90	460, 760	13
	Pyrolysis $(CH_3)_3CCH_2ONO$	6.70	6.92	450	11
$(CH_3)_2C-C\equiv N$	Pyrolysis AIBN	--	8.56	--	14
	Pyrolysis 	7.21	7.46	--	15, 16
	Pyrolysis 	7.15	7.40	--	15, 16
	Pyrolysis 	6.84	6.84	--	16
	Pyrolysis 	6.83	6.83	--	16

Table I (continued)

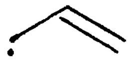
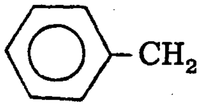
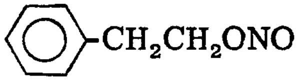
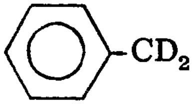
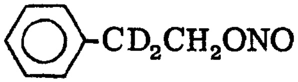
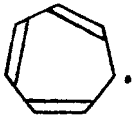
Species	Source	IP (eV)		Vibrational Structure (cm^{-1})	Reference
		A	V		
	Pyrolysis CH_2=CHCH$_2$CH$_2$ONO	8.13	8.13	420	17
	Pyrolysis bibenzyl	7.43^c	7.43	--	14
	Pyrolysis 	7.20^c	7.20	560	17
	Pyrolysis 	7.22^c	7.22	480	17
	Pyrolysis bitropyl	6.28^c	6.28	1420	18
$(CF_3)_2NO\cdot$	Pyrolysis $(CF_3)_2NOH$	--	10.7^c	--	19

Table I (continued)

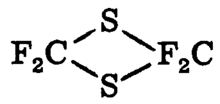
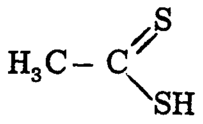
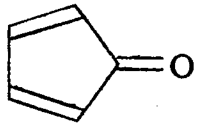
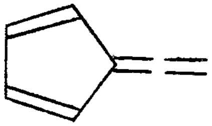
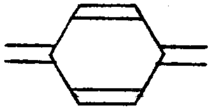
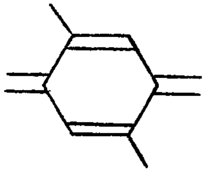
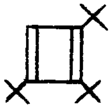
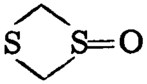
Species	Source	IP (eV) A	IP (eV) V	Vibrational Structure (cm^{-1})	Reference
Closed Shell					
H_2CS	Pyrolysis	9.34^c	9.34	1000	20
	CH_3SSCH_3				
	Pyrolysis	9.38^c	9.38	935	21
	CH_3SCl				
F_2CS	Pyrolysis	10.45^c	10.62	1380, 450	22
					
CHClO	Reaction	11.51^c	11.61	610,830,1390	23
	$HCOOH + PCl_5$				
CH_2NH	Pyrolysis	~10.0^c	10.52	--	24
	CH_3NH_2				
$H_2C{=}C{=}S$	Pyrolysis	8.89^c	8.89	1450, 700	25
					

Table I (continued)

Species	Source	IP (eV)		Vibrational Structure (cm^{-1})	Reference
		A	V		
	Pyrolysis Orthoquinone	--	9.49^c	--	26
	Pyrolysis Phtalide	8.22^c	8.22	?	27
	Pyrolysis [2.2]paracyclophane	7.87^c	7.87	?	28
	Pyrolysis tetramethyl [2.2]paracyclophane	7.58^c	7.58	?	29
	Pyrolysis tri-<u>tert</u>- butylcyclopentadienone	--	6.83	?	30
$CH_3N{=}NH$	MWD CH_3NHNH_2	8.8^c	9.57	--	31
H_2CSO	Pyrolysis 	?	10.23^c	?	32

Footnotes to Table I

[a] MWD = Microwave discharge.

[b] Hot bands may contribute significantly to this spectrum.

[c] Higher IPs of the transient were identified.

Table II. Photoelectron data for open- and closed-shell inorganic transient molecules.

Species	Source	IP (eV)		Vibrational Structure (cm^{-1})	Reference
		A	V		
Open Shell					
H	MWD[a] H_2	13.61	--	--	4
N	MWD N_2	13.62	--	--	4
O	MWD O_2	14.55[b]	--	--	4
F	MWD CF_4	17.47[b]	--	--	33
Cl	MWD Cl_2	12.97[b]	--	--	33
Br	MWD Br_2	11.81[b]	--	--	33
I	MWD, reaction $Br + I_2$	10.43[b]	--	--	33
OH	MWD, reaction $H + NO_2$	13.01[b]	13.01	2950	34
OD	MWD, reaction $D + NO_2$	?	?	2260	34
ClO	MWD, reaction $Cl + O_3$	10.83	10.96	1040	35
BrO	MWD, reaction $O + Br_2$	10.29	10.29	830	36
NS	MWD NSCl Pyrolysis S_7NH	8.87	8.87	1415	37
SO	MWD SO_2	10.29[b,d]	10.29	1360	38

Table II (continued)

Species	Source	IP (eV) A	IP (eV) V	Vibrational Structure (cm^{-1})	Reference
S_2	heating flowers of sulfur	9.38[b, d]	9.38	770	39
ClO_2	?	10.37[b]	10.5	1014, 520	19
SiF_2	heating SiF_4 over Si	-	11.08[b]	?	40
	heating CaF_2 + Si	10.78[b]	11.18	350	41
NF_2	pyrolysis N_2F_4	11.63[b]	12.1	1250	19
SO_3F	pyrolysis $S_2O_6F_2$	12.85[b]	12.85	1220	19
Closed Shell					
CS	MWD CS_2	11.33[b]	11.33	1290	42
		11.33[b]	11.33	1330	43
		11.34[b]	11.34	1380	44
SiO	heating $(SiO)_x$	11.61[b]	11.61	-	45
GeO	heating Ge + GeO_2 + Ar/He	11.25[b,e]	11.25	830	46
PN	pyrolysis P_3N_5	11.85[b]	11.85	1200	47
		11.88[b]	11.88	1230	48

Table II (continued)

Species	Source	IP (eV)		Vibrational Structure (cm^{-1})	Reference
		A	V		
P_2	RF induction heating, P_4	10.53^{b,d}	10.61^{d}	670	49
TlCl	Vaporization TlCl	9.70^{b,f}	10.38^{f}	-	50
TlBr	Vaporization TlBr	9.14^{b,f}	9.83^{f}	-	50
TlI	Vaporization TlI	8.47^{b}	8.91	-	50
O_3	-	12.44^{b}	12.75	650	7
		12.53^{b}	12.75	630	51
S_2O	$SO_2Cl + Ag_2S$, or	?	10.52^{b}	?	52
	MWD SO_2	10.53^{b}	10.59	480	53
NSCl	pyrolysis $N_3S_3Cl_3$	10.61^{b}	10.95	-	54
HBS	H_2S over B, heated	11.11^{b}	11.23	955	55
FCN	MWD cyanuric fluoride	13.34^{b}	13.65	2100	56
Tl_2F_2	vaporization Tl_2F_2	?	9.96^{b}	-	57
HN=NH	MWD N_2H_4	9.59^{b}	10.02	1180	31
DN=ND	MWD N_2D_4	9.61^{b}	10.10	1020	31
N_2S_2	S_4N_4 over Ag wool	10.41^{b}	10.52	470, 810	58

Table II (continued)

Species	Source	IP (eV) A	IP (eV) V	Vibrational Structure (cm^{-1})	Reference
HNSO	$Cl_2SO + NH_3$	?	11.60^b	?	59
NCN_3	BrCN over activated NaN_3	11.00	11.00	1900, 1120, 800	60
NCNCO	pyrolysis AgNCO	11.49	11.75	2130, 540	60
S_8	sulfur vapor	?	9.23^b	-	61

[a] MWD = microwave discharge

[b] Higher IPs of the transient species were identified.

[c] Spin-orbit splittings were resolved. The IP listed corresponds to ionization from the $X\,^2\Pi_{\frac{1}{2}}$ state of ClO.

[d] Spin-orbit splittings were resolved. The IP listed corresponds to ionization to the $^2\Pi_{\frac{3}{2}}$ state of the ion.

[e] This is the ionization energy to the (assigned) $\tilde{X}$ state of the ion. The adiabatic IE to the A state is lower - 10.92 eV. The two curves cross at a point along r_e approximately midway between 1.643 and 1.783 Å, so the vertical IEs are in the order $\tilde{A} > \tilde{X}$.

[f] These IPs are the lowest of this species, but correspond to formation of the first excited state of the ion. The ground state is a sharp band imbedded in the broad band arising from the excited state.

Table III. Photoelectron Data for Excited Molecules.

Species	State(s)	Source	Reference
$O_2{}^*$	$^1\Delta_g$, $^3\Sigma_g^-$	MWD O_2[a]	5, 62
$N_2{}^\dagger$	$v'' = 0 - 7$	MWD N_2	63
$H_2{}^\dagger$	$v'' = 0 - 2$	MWD H_2	63

[a] MWD = microwave discharge

Table IV. Photoelectron Data for van der Waals Molecules.

Species	Source	IP (eV)		Reference
		A	V	
Ar_2	SSE[a] Ar	14.44[b, c]	15.55	64
Kr_2	SSE Kr	12.87[b, d]	13.76	64
Xe_2	SSE Xe	11.13[c, d]	11.85	65

[a] SSE = supersonic expansion.

[b] Calculated from Ar_2^+ dissociation energy. Not observed because of an exceedingly low Franck-Condon factor for the O-O transition.

[c] Higher IPs were identified.

[d] Taken from a Photoionization Mass Spectrometric measurement. Adiabatic IP not observed due to poor Franck-Condon overlap for the 0-0 transition.

Lineberger and coworkers, are beyond the scope of the present work, which includes only neutral species. They provide, however, an important complement to the free radical photoelectron spectra.

A wide variety of information is obtained in these experiments. With the exception of most of the organic free radicals,[66] several photoelectron bands are observed for the transient species, allowing identification of some of the excited states of the corresponding ions. Analysis of the first photoelectron band provides both adiabatic and vertical ionization potentials, which can be used to determine various thermochemical quantities such as the heat of formation of either the transient or its ion, homo- and heterolytic bond dissociation energies and absolute proton affinities (where applicable). The shape of the first photoelectron band, especially when one or more vibrational progressions are resolved, can give important information on structural differences between the neutral transient and its ion. This in turn allows characterization of the extent of delocalization of the highest energy electron in the neutral species. Similar information can sometimes be extracted from the higher photoelectron bands if they exhibit vibrational structure. Finally, primary decomposition and reaction pathways of the transient species are readily identified using photoelectron bands of product species appearing in the spectrum. This is an aspect of the photoelectron spectroscopy of transients, especially reactive intermediates, that has not yet been extensively pursued.

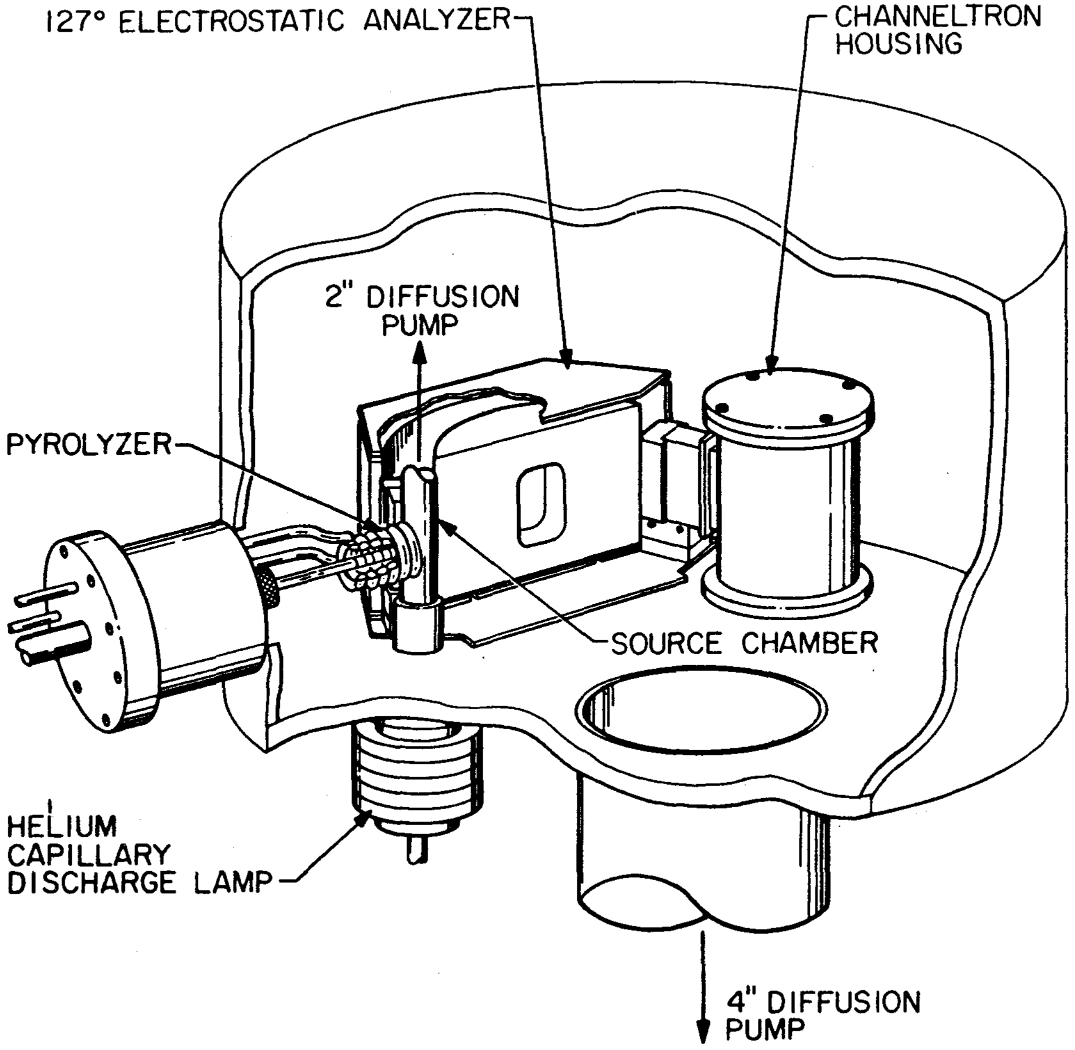
Interpretation of the data to obtain structural information is heavily dependent on the availability of independent data on either the transient or its ion. These data come mainly from theoretical calculations, esr experiments and optical spectroscopy of matrix-isolated species. In general, except for diatomics, the few data available are inadequate for any quantitative structural information to be extracted from the photoelectron spectra. In view of this situation a philosophical point should be made. In a somewhat different context, Dr. L. Kaplan has written "Most of the large amount of such work, although fruitful, has been executed myopically. Lines of reasoning and experimentation have been extended far beyond any secure base of knowledge and understanding."[67] This statement could easily have been made as a critical evaluation of efforts to assess the extent of structural change on ionization in polyatomic chemical transients. The counterargument presented here is that, although only qualitative conclusions can be drawn in most cases (perhaps even so vague or speculative as to be useless), these conclusions serve the important purpose of drawing attention to inadequacies in present knowledge and provide hypotheses for testing in future research. It is in this spirit that the work presented in this thesis and elsewhere[17, 68] is intended to be read.

The main topic of this thesis is the photoelectron spectroscopy of alkyl free radicals produced by pyrolysis of the corresponding alkyl nitrites. Other experiments performed on the instrument described below include a search for vibrational excitation in nitrogen extruded during the thermolysis of strained azo compounds[69] and HN_3;[70] and attempts to observe CH_2,[70] trimethylenemethane,[71] triplet acetone,[70] chain reactions ($H_2 + O_2$) and 4-center elimination reactions (CH_2FCH_3).[72] With the exception of the azo project, all of these experiments yielded ambiguous or negative results because of the chemical complexity of the systems and/or unsuitability of the instrumentation. The nitrite experiments were, however, extraordinarily successful, providing a great deal of new information on the simple alkyl free radicals.

A schematic of the spectrometer is shown in Figure 1. The instrument is a photoelectron spectrometer of standard design which has been specifically modified to study the products of gas phase pyrolyses. The differentially pumped source chamber, 127° electrostatic analyzer, and Channeltron electron multiplier are situated on a stainless steel baseplate in a high vacuum chamber. The capillary discharge lamp, located directly underneath the source chamber, is separated from the main vacuum chamber by a stage of differential pumping. The lamp can be operated with both He and Ne gases. The analyzer is protected from magnetic fields by a mumetal shield and a set of six Helmholtz coils. Sample gases are introduced into the source chamber through a stainless steel inlet system divided into three sections. Two of these are connected to the bottom of the source chamber and are used for calibrant gases (usually argon) and samples at room temperature. The third enters the vacuum chamber through the side wall. It consists of a 3 mm ID quartz tube fitted to a stainless steel flange. This tube is used for pyrolysis. A 2 cm long section at the free end of the tube is wrapped with double-stranded Semflex

Figure 1

Schematic of the photoelectron spectrometer used in these experiments.


127° ELECTROSTATIC ANALYZER
CHANNELTRON HOUSING
2" DIFFUSION PUMP
PYROLYZER
SOURCE CHAMBER
HELIUM CAPILLARY DISCHARGE LAMP
4" DIFFUSION PUMP

heater wire insulated with MgO and an Iconel outer sheath. A chromel-constantan thermocouple is wedged between the sheath and the quartz tube to monitor the temperature. Constant temperatures of up to 1000° C can be maintained for hours. The analyzer is protected from black-body radiation by a water-cooled copper shield surrounded the hot section. The tip of the quartz tube is inserted through an aperture in the side of the source chamber, such that the hot gases traverse a 0.75 cm path before intersecting the photon beam at a 90° angle. Electrons ejected normal to this plane are energy analyzed and detected, and the resulting spectrum is accumulated in a Tracor-Northern NS-570A multichannel scaler with 4K memory.[73] Details of particular experiments are given in the Experimental sections of each chapter.

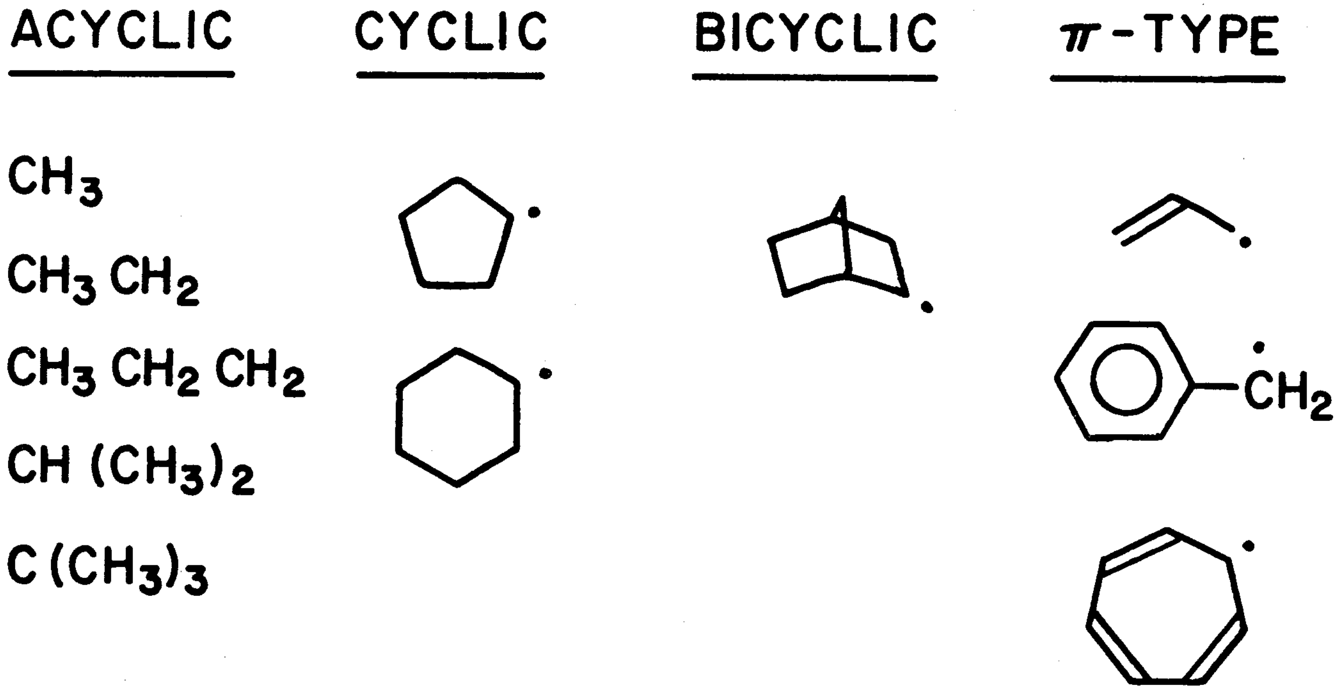
The results of the present experiments can be classified in two independent ways. The first is a grouping of hydrocarbon free radicals according to their IPs. This traditional manner of looking at alkyl radicals yields roughly the expected ordering of IP (tertiary center) $<$ IP (secondary center) $<$ IP (primary center) $<$ methyl radical. Furthermore, with the exception of some of the conjugated π-type radicals and 2-norbornyl radical, a characteristic range of IPs can be established for each type of center since it has been found that the IP is relatively insensitive to the size of the radical. Thus, primary alkyl radicals have IPs in the range 8.0-8.4 eV, secondary radicals $\sim$7.0-7.4 eV, and tertiary radicals $\leqslant$ 6.7 eV. This can be used for diagnostic purposes when studying, for example, thermolyses of alkyl radicals. The exceptions are readily identifiable as special cases:

benzyl and cycloheptatrienyl radicals both give aromatic ions, and both 2-norbornyl radical and cation are exceptionally stable. All three radicals have unusually low first IPs, as expected.[16-18]

On comparison of the shapes of the first photoelectron bands, a second classification arises, as shown in Figure 2. Each of the four groups exhibits a unique and characteristic photoelectron band, which can be interpreted in terms of geometry changes on ionization common to the members of each group. Thus, the acyclic aliphatic alkyl radicals are thought[11, 12] to undergo a shortening of the C–C bonds, excitation of internal rotations and conversion from a nonplanar to a planar trigonal site on ionization.[74] The cyclic aliphatic alkyl radicals have only broad, smooth photoelectron bands,[15, 16] possibly attributable to the fact that both the ions and radicals can exist in several different nondegenerate conformations. Transitions between the various pairs of neutral and ionic structures would produce overlapping bands tending to make vibrational structure (if present) unresolvable. The conjugated π-type radicals, on the other hand, have very sharply resolved photoelectron bands exhibiting at most two vibrational progressions.[17, 18] Their adiabatic and vertical ionization potentials coincide, indicating only minimal geometry change occurs on ionization. The presence of vibrational structure signals a change in force constants, but the precise modes involved have not been determined unambiguously. Finally, 2-norbornyl radical[16] is at present the only member of the bicyclic group. It undergoes essentially no geometry change on ionization, indicating both neutral and ion to be rigid. Vibrational structure is not clearly resolved, possibly

Figure 2

Classification of alkyl radicals according to their first photoelectron bands. A discussion is given in the text.


ACYCLIC
CYCLIC
BICYCLIC
π-TYPE
CH_3
CH_3CH_2
$CH_3CH_2CH_2$
$CH(CH_3)_2$
$C(CH_3)_3$
$\dot{C}H_2$

due to the presence of secondary thermolysis products, one of whose first photoelectron band partially overlaps that of 2-norbornyl radical. Whether or not the band shape of 2-norbornyl radical is typical of rigid bi- and tricyclic alkyl radicals will be investigated in future work.

Deuterium substitution at the radical center will cause the observed IP of that radical to decrease, stay the same, or increase, depending crudely on whether the unpaired electron was antibonding, nonbonding, or bonding overall, respectively.[17] Isotopic data are available for $CH_3(CD_3)$,[10] $CH_3CH_2(CH_3CD_2)$,[11] benzyl radical (benzyl-α-d_2 radical),[17] and 2-norbornyl radical (2-norbornyl-2-d radical).[16] It was found that the IPs of saturated species all decreased on deuteration, indicating that the unpaired electron has antibonding character overall in these radicals. Deuterium substitution in benzyl radical, however, showed that the unpaired electron has bonding character overall.

Although the list of transient systems studied using PES is remarkably long considering the relatively small number of laboratories involved, much remains to be done. Oxygen-, sulfur-, silicon- and nitrogen-centered alkyl radicals are essentially unexplored. α- and β-heteroatom substitution in carbon-centered radicals has not been studied. Few of the higher IPs of alkyl radicals have been determined. Only a small sample of inorganic and organometallic radicals have been investigated.

The two main impediments to progress are low-resolution spectrometers, and the lack of good precursors and methods of generation. Improvements are being made, however. A design has been published for a versatile, fast pumping photoelectron spectrometer, specifically designed for use in the study of transients.[75] Phase-sensitive detection of transients produced in a modulated microwave discharge[62] has allowed extraction of the pure transient spectrum. A pulsed, inductively heated, high-temperature furnace furnace has recently been constructed.[76] This source will allow study of transients produced by pyrolysis in reactions too endothermic to be observed using a resistively heated furnace. Sources not now in use, but which are likely to be developed in the next few years are supersonic beams of free radicals, flames, laser photolysis and flash photolysis. Application of photoion-photoelectron coincidence and threshold photoelectron techniques will allow highly accurate (± .005 eV) determination of first and higher IPs, and assessment of the role of hot bands and autoionization in the spectra of the transients.

With these improved experimental techniques, application of PES to the study of chemical reactions producing transient species, as well as the chemistry of the transients themselves, will become more widespread. Some studies of the pyrolysis of various organic systems have already been reported.[69,77-79] The first direct observations of thermal decomposition pathways of alkyl free radicals are discussed in this thesis.[12,15] Studies of identities, reactions and internal energies of species produced in flames and photolytic cells are expected to be especially fruitful, directly providing information which can only be had laboriously using other techniques.

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CHAPTER II

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

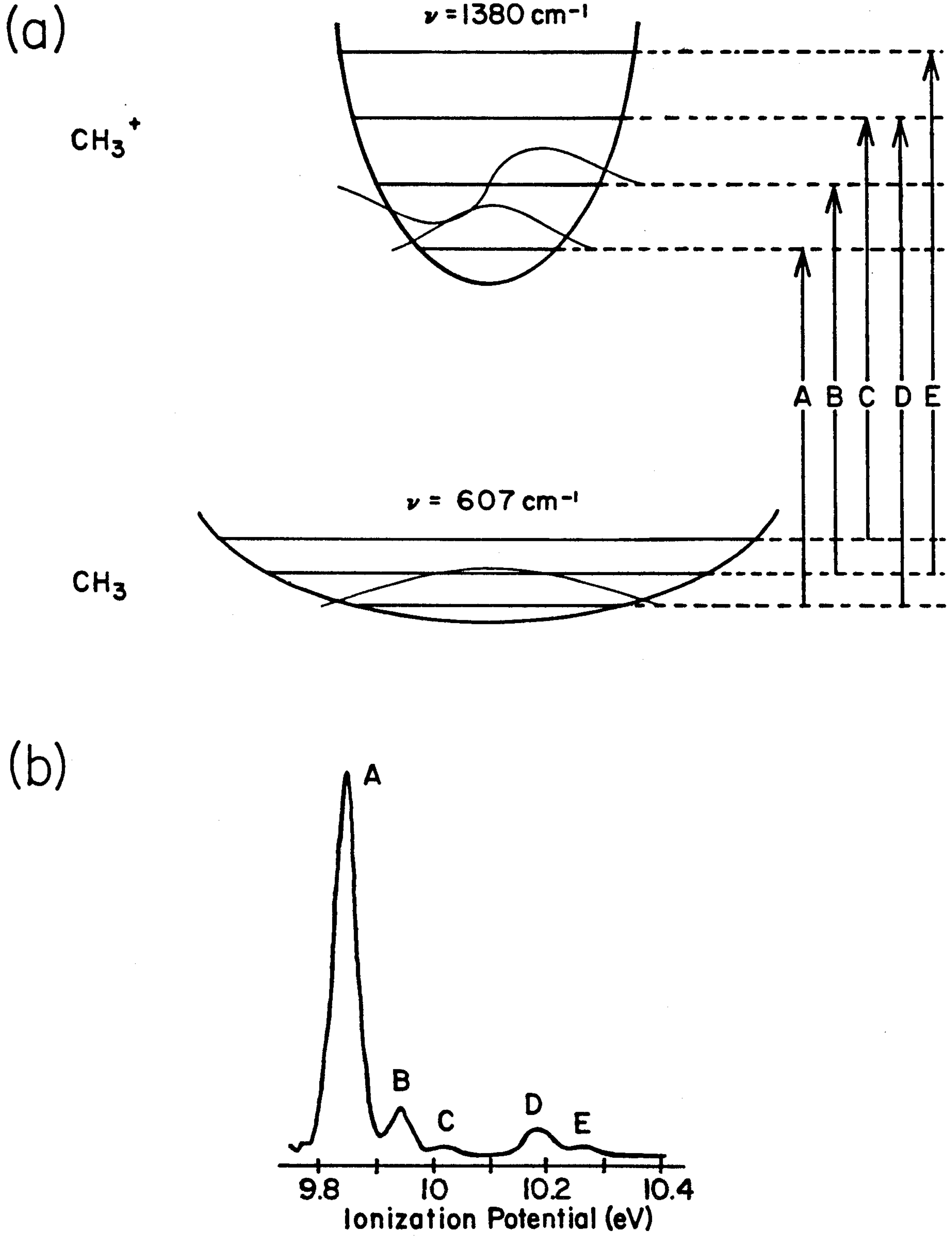
The first photoelectron bands of the series of simple alkyl free radicals CH_3, CH_3CH_2, CH_3CD_2, CH_3CHCH_3, and $C(CH_3)_3$ have been obtained. The adiabatic and vertical ionization potentials, respectively, are 9.84 ± 0.02 eV for methyl radical, 8.39 ± 0.02 and 8.51 ± 0.02 eV for ethyl radical, 8.38 ± 0.02 and 8.50 ± 0.02 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.

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)
ν =1380 cm⁻¹
CH_3^+
A B C D E
ν = 607 cm⁻¹
CH_3
(b)
A
B
C
D
E
9.8
10
10.2
10.4
Ionization Potential (eV)

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 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 cm^{-1} (gas phase),[22] 541 cm^{-1},[20] tentatively 375 cm^{-1},[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:

$$\begin{aligned} RCH_2ONO &\rightarrow RCH_2O + NO \\ RCH_2O &\rightarrow R + CH_2O \end{aligned} \qquad (1)$$

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 unlabelled alcohols were obtained from Aldrich.

1-propanol-2,2-d_2 was prepared from propionic acid-2,2-d_2, which was labelled by deuterium exchange in a basic medium.[32]

0. 225 moles of sodium propionate were 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% labelled. 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 HeI and NeI 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 sec^{-1}. The energy scales were calibrated using the HeIα and HeIβ bands of CH_2O, NO, and Ar. The resolution for these experiments is 30-35 mV. 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 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 Figs. 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-methyl propyl nitrite and 2, 2-dimethyl propyl nitrite are presented in Figs. 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 Fig. 4a. A somewhat different spectrum of this species was reported in a preliminary communication.[34] Repetition of the early work using NeI radiation showed that the feature assigned to be the adiabatic ionization potential was actually due to the HeIβ ionization of one of the NO bands. 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.

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 2

The HeI spectrum of 2-methyl propyl nitrite.

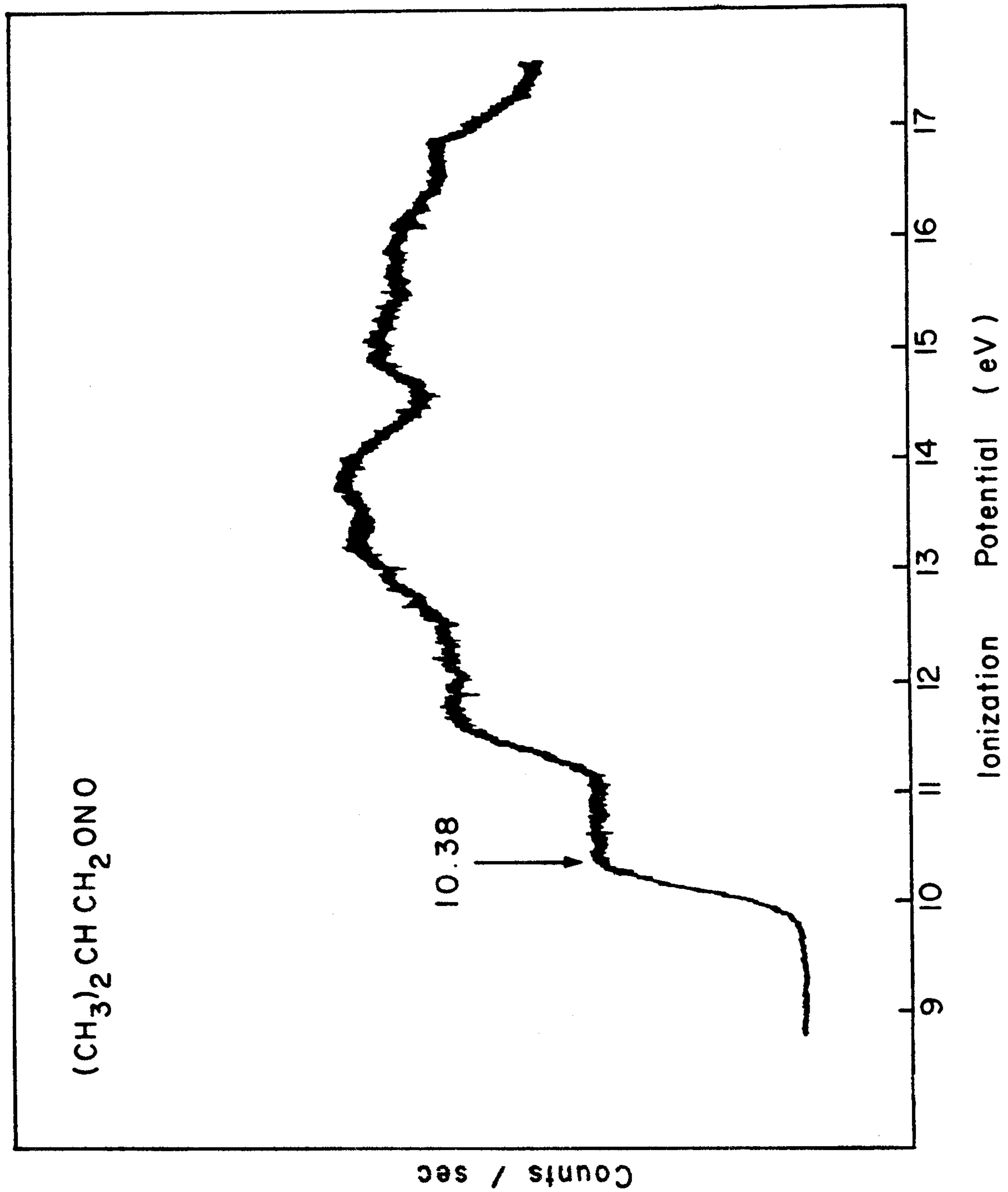

$(CH_3)_2CHCH_2ONO$
10.38
9
10
11
12
13
14
15
16
17
Ionization Potential (eV)
Counts / sec

FIGURE 3

The HeI spectrum of 2, 2-dimethylpropyl nitrite.

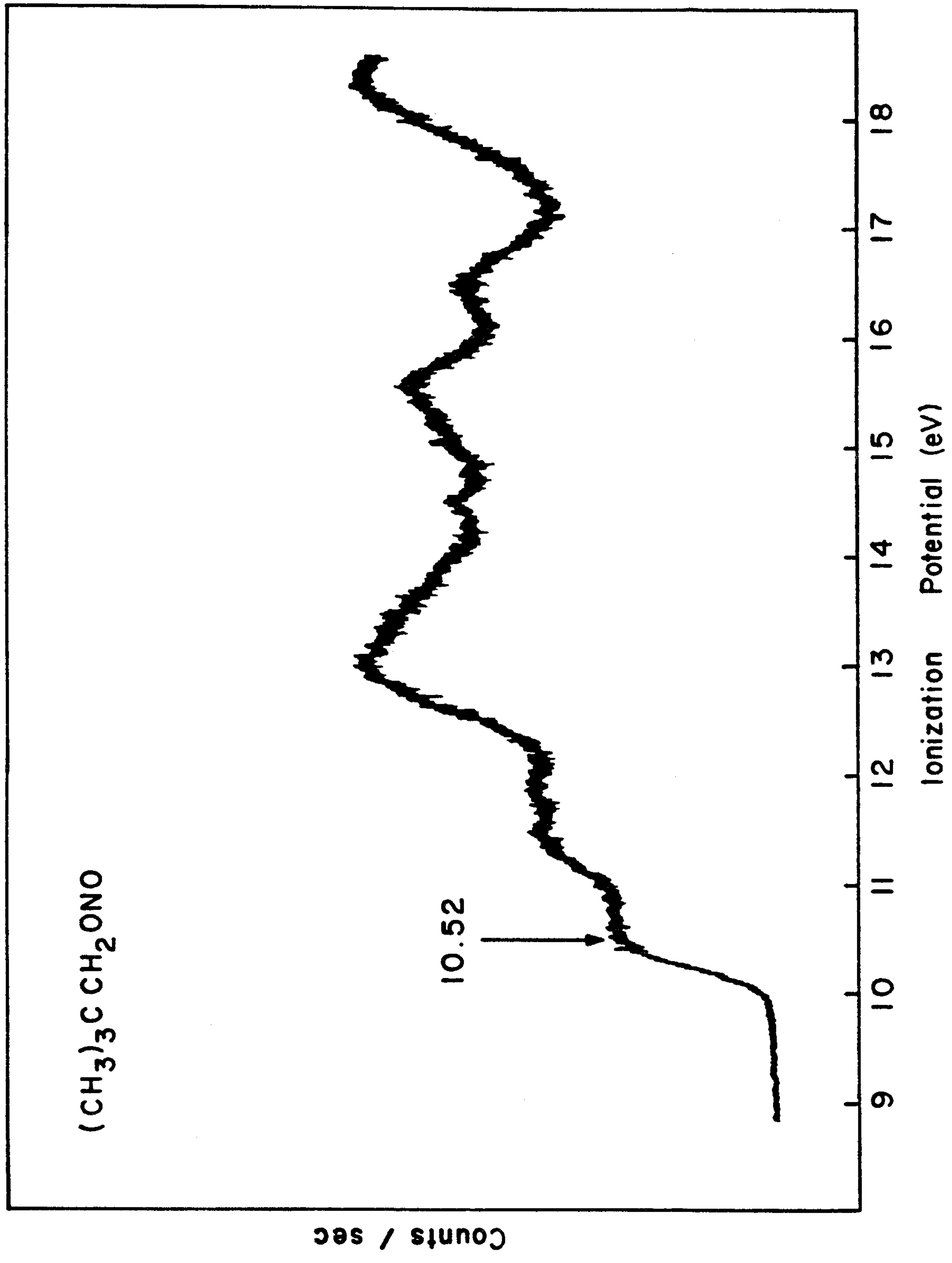
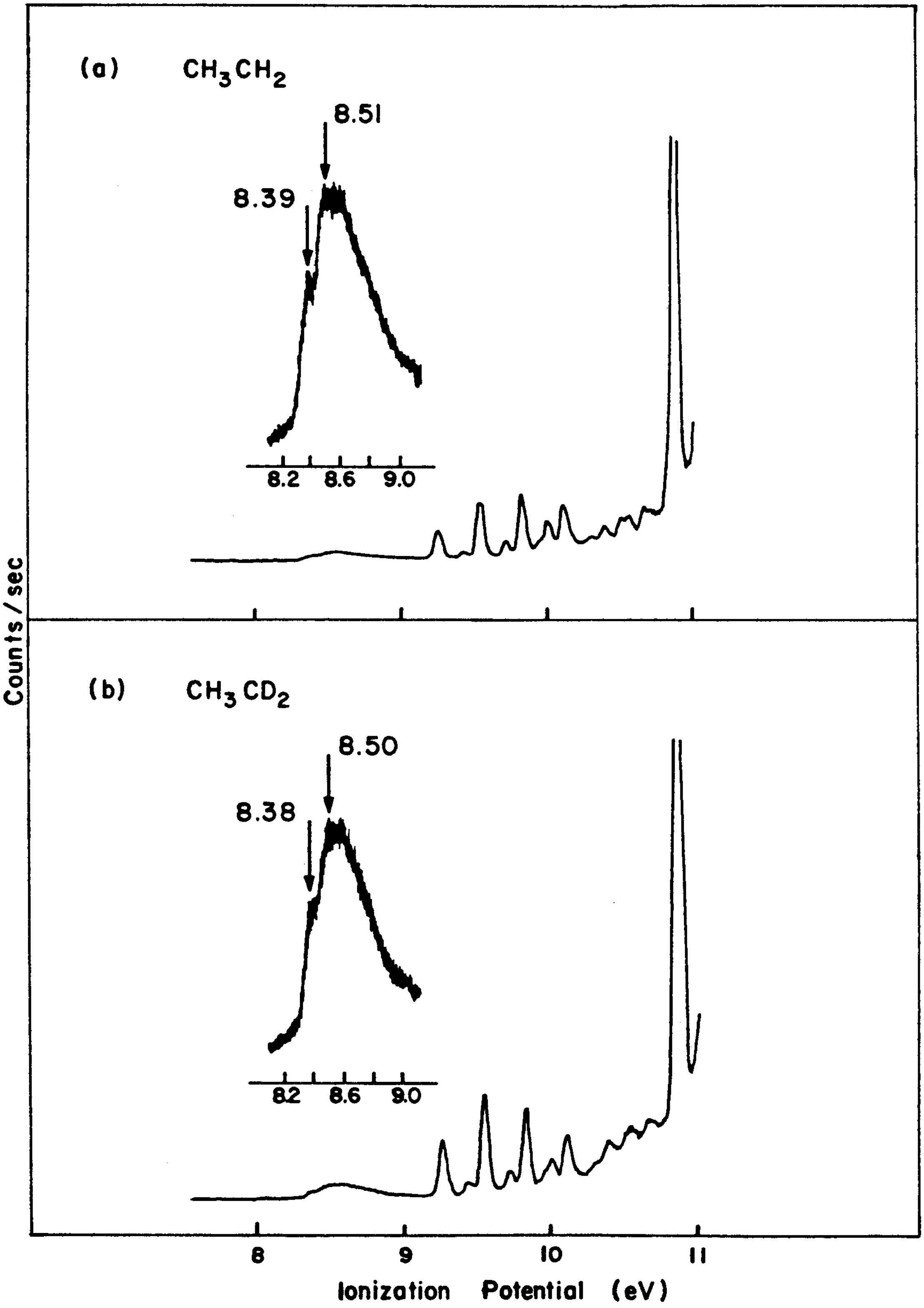

(CH$_3$)$_3$C CH$_2$ONO
10.52
9
10
11
12
13
14
15
16
17
18
Ionization Potential (eV)
Counts / sec

FIGURE 4

The NeI spectra of ethyl radicals. Bands from 9.27 - 10 eV arise from NeI α and β ionization of NO. CH_2O is at 10.884 eV. Inserts show the radical bands in greater detail. The relatively minor contribution from NeI α ionization has not been subtracted from them. Their main effect is to broaden the peak maxima compared to those obtained with HeI light. (a) The spectrum of ethyl radical. (b) The spectrum of ethyl-1, 1-$\underset{\frown}{d}_2$ radical.


(a) CH_3CH_2
8.51
8.39
8.2
8.6
9.0
(b) CH_3CD_2
8.50
8.38
8.2
8.6
9.0
Counts / sec
8
9
10
11
Ionization Potential (eV)

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

$CH_3CHCH_3\cdot$ The first photoelectron band of isopropyl radical is shown in Fig. 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}).

$C(CH_3)_3\cdot$ The data obtained for *tert*-butyl radical are presented in Figs. 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 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

FIGURE 5

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

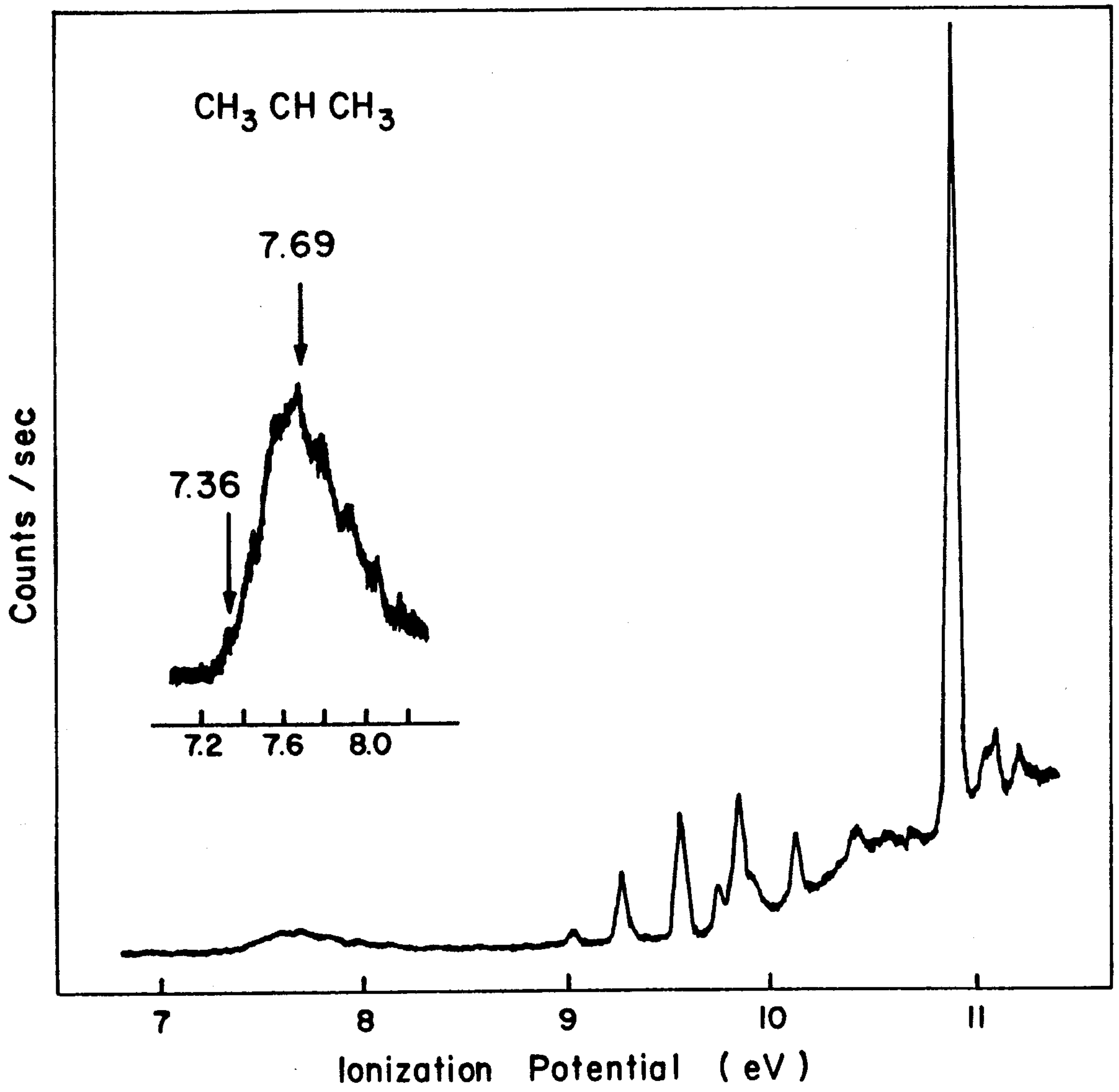

CH_3 CH CH_3
7.69
7.36
7.2
7.6
8.0
Counts / sec
7
8
9
10
11
Ionization Potential (eV)

FIGURE 6

The HeI 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.

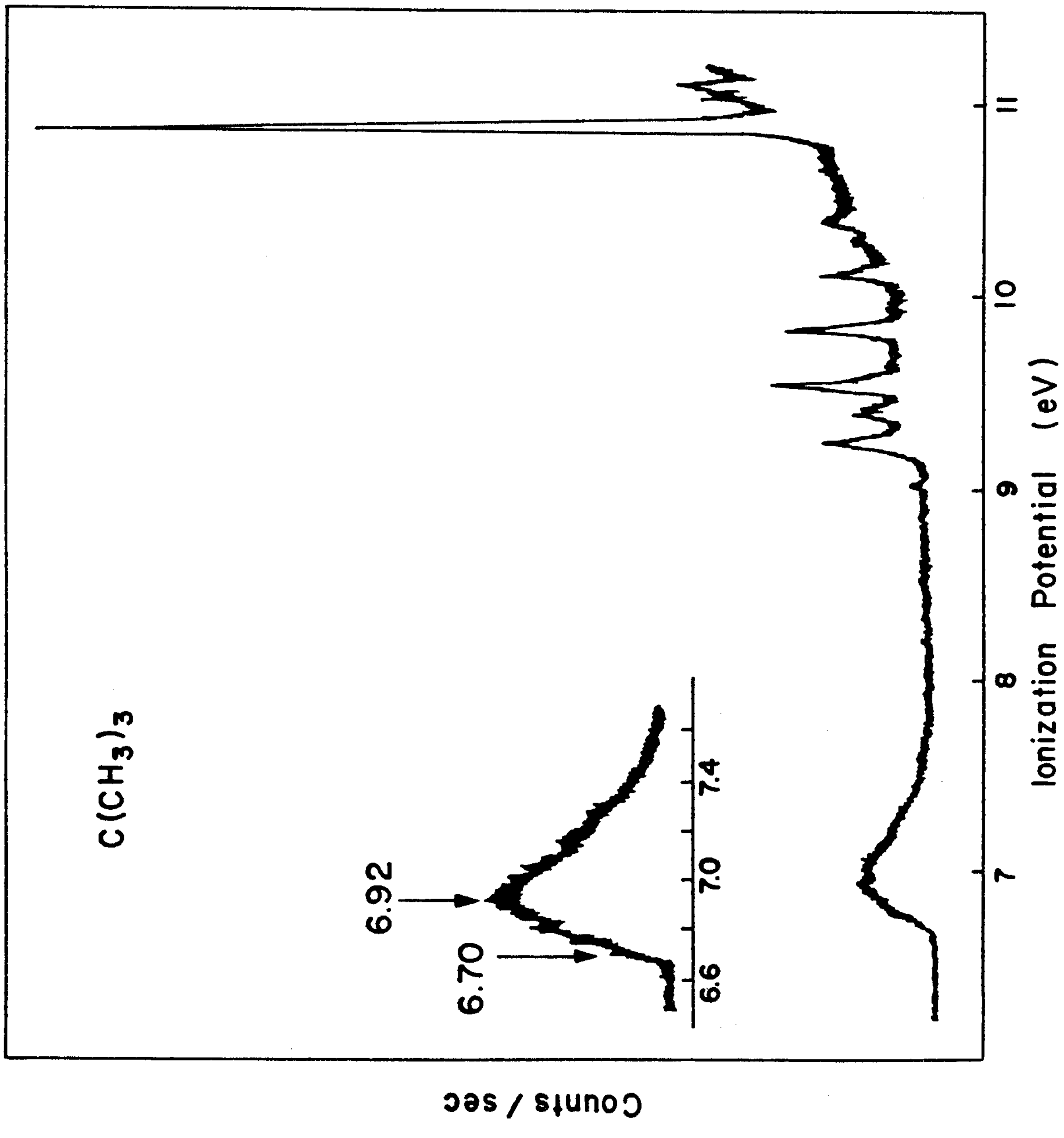
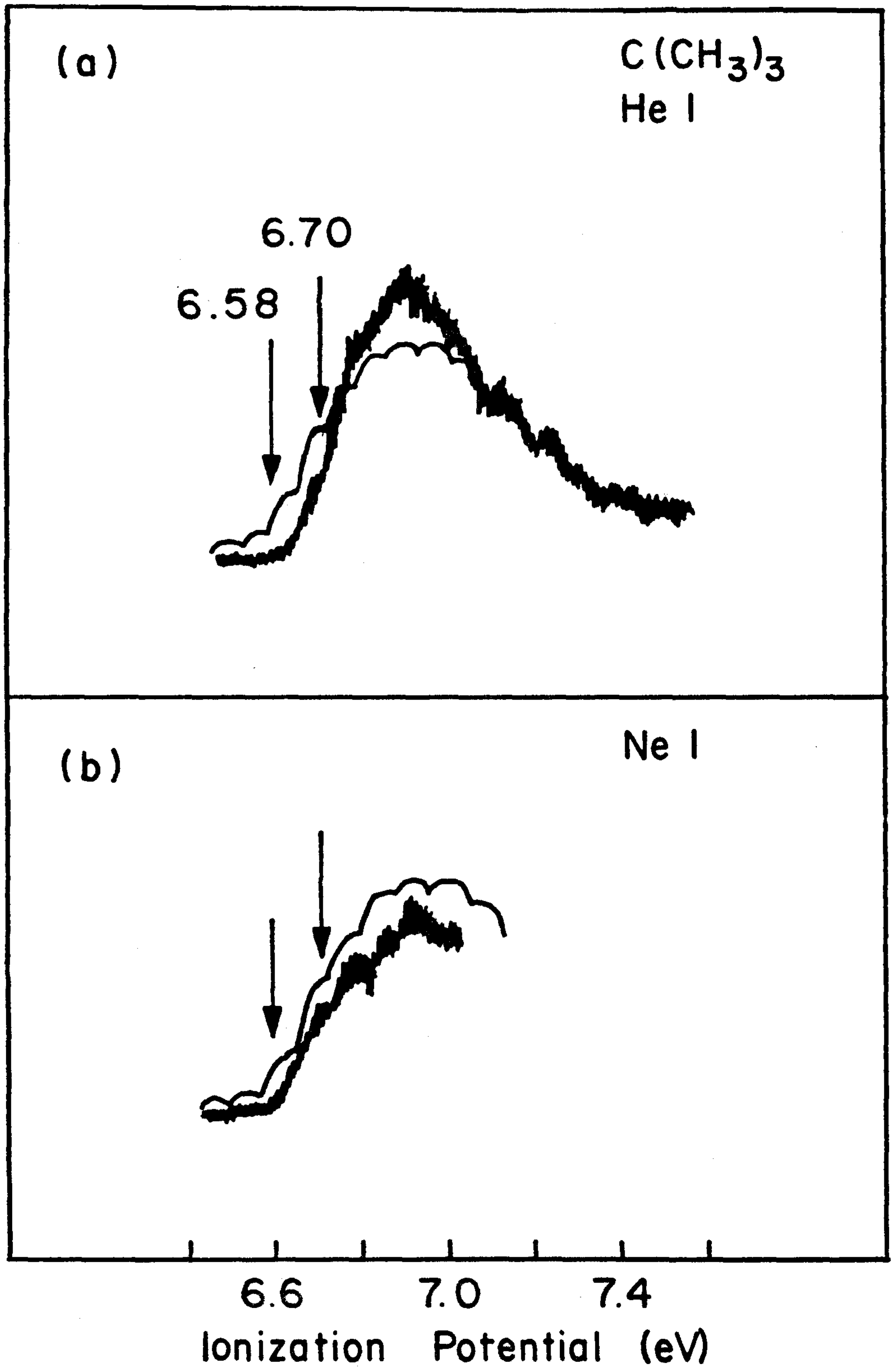

C(CH$_3$)$_3$
6.92
6.70
6.6
7.0
7.4
7
8
9
10
11
Ionization Potential (eV)
Counts / sec

FIGURE 7

Comparison of our tert-butyl spectrum with the higher temperature NeI 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 HeI data of this work. (b) Overlay with the NeI results of this work.


(a)
$C(CH_3)_3$
He I
6.70
6.58
(b)
Ne I
6.6
7.0
7.4
Ionization Potential (eV)

to the earlier spectrum is shown in Fig. 7. It can be seen that hot bands, which Jonathan and coworkers 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 Fig. 7, although it appears to grow in at $\gtrsim 650°$ 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 HeI light was used in the present work. However, using NeI radiation, a progression of ~ 450 cm^{-1} appeared (see Fig. 7b). The structure on the high ionization energy side of the band was obscured by overlapping of NeIα and NeIβ spectra.

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 labelling 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 converge[40, 41] (see Table II). However, recent work[42] has yielded values revised upwards 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]

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]
			8.4[d]
CH_3CH_2	25.7[c]		9.3[g]
	28.5[e]		9.5[h]
CH_3CHCH_3	17.6[c,d]		12.1[e]
	20.5[e]		

---

[a] All quantities in kcal/mol. Error limits are ± 1-2 kcal/mol.

[b] Ref. 62.

[c] Ref. 40.

[d] Ref. 41.

[e] Ref. 42.

[f] Ref. 47.

[g] Ref. 63.

[h] Ref. 64.

The ionic equilibria (2) and (3),[44, 45] which yield reaction

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

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

enthalpies of -0.03 ± 0.24 kcal/mol[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 kcal/mol (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 kcal/mol 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

Table III. Recommended Thermochemical Data[a]

R	$\Delta H_f(R\cdot)$	$\Delta H_f(R^+)$[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.

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/mole. 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.

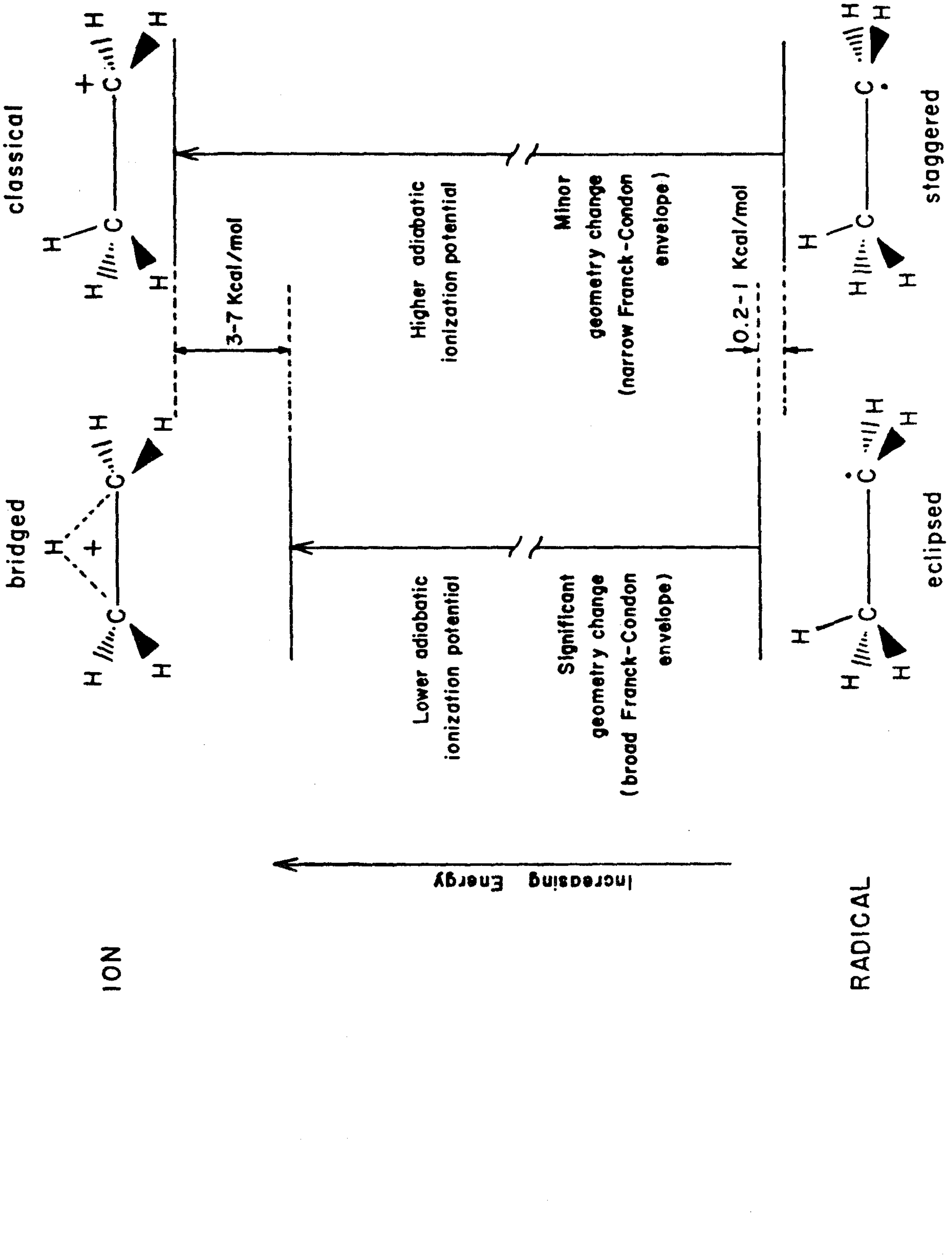
As noted in the introduction, methyl radical undergoes essentially no geometry change on ionization. Its photoelectron spectrum exhibits a double quantum transition in the out-of-plane bending mode, ν_2, indicating that a planar radical is becoming a planar ion.[3] The frequency of the ν_2 mode is much larger in the ion (1380 cm^{-1})[3] than in 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 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 Fig. 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

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.)


classical
bridged
ION
RADICAL
staggered
eclipsed
3-7 Kcal/mol
0.2-1 Kcal/mol
Higher adiabatic ionization potential
Minor geometry change (narrow Franck-Condon envelope)
Lower adiabatic ionization potential
Significant geometry change (broad Franck-Condon envelope)
Increasing Energy

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° 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 $900 \pm 100\ \mathrm{cm}^{-1}$ is in disagreement with the results of ESR experiments, which yield a barrier of $\lesssim 160\ \mathrm{cm}^{-1}$. 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 <u>tert</u>-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 reference 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 <u>tert</u>-butyl cation.[39]

It should be noted that, even if the isopropyl and <u>tert</u>-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 cm^{-1}[22] and 1380 cm^{-1}[3]) and $C(CH_3)_3$ and $C(CH_3)_3^+$ (< 200 cm^{-1}[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_3, 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 upwards from its old value of 202.0 kcal/mol to 208.4 kcal/mol. Reasonable error limits are ± 2 kcal/mol. Additional experiments are under way 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 bandshapes are broad and featureless.[60]

Deuterium labelling 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 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 bonds 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 under way 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.

Acknowledgments

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CHAPTER III

On the Conformations of the Simple Alkyl Free Radicals

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Abstract

A balance of several electronic interactions is thought to govern the equilibrium structures of the alkyl substituted carbon-centered radicals. However, one interaction has not been considered previously. This is the direct repulsion between the substituent bond pairs and those of the radical center. The effect of these repulsive forces on radical geometries is discussed. Examples are drawn from theoretical and experimental work on ethyl and tert-butyl radicals.

The effect of substituents on the conformation of a radical center is a subject which has received much attention in the literature. It has been proposed that the planarity of a radical center is determined by the electronegativity of the substituents bonded to it (1, 2). This is a mechanism primarily involving the σ framework of the molecule. Substituents less electronegative than the radical center will cause it to be planar, while those with higher electronegativity induce strongly pyramidal structures. Another effect proposed to account for radical conformations is conjugative destabilization (3, 4), where interactions between substituents with lone pairs or σ orbitals favor pyramidal radical centers. Finally, interactions between the unpaired electron on the radical center and substituent orbitals of π symmetry can stabilize or destabilize planar structures (5).

These models have been applied to various radicals, rationalizing known structures and predicting unknown ones with varying degrees of success. Among those radicals whose geometries are not well known are the alkyl radicals CH_3CH_2, CH_3CHCH_3, and $C(CH_3)_3$. None of the models described above adequately treats the effect of successive methyl substitution on a carbon-centered radical.

Electron spin resonance (ESR) and infrared (IR) spectroscopy provide most of the available information on the structure of the alkyl radicals. All three species have essentially free rotation about the C–C bonds (6). The α C–H stretches in ethyl and isopropyl radicals are characteristic of sp^2-hybridized centers, but unlike olefins such as ethylene and propylene, these centers exhibit low out-of-plane bending frequencies (7). The most obvious conclusion is that the alkyl radical centers are planar, yet easily deformed. However, the temperature dependence of the H and ^{13}C hyperfine splitting constants in tert-butyl radical is not strongly supportive of this simple picture. Two studies were interpreted as showing this species to be nearly tetrahedral with a barrier to inversion of 0.6 kcal/mol (8, 9). It was subsequently pointed out (10) that the observed temperature dependence is highly influenced by the nature of the solvent or matrix employed. The matrix effect was confirmed in recent liquid phase studies (11), which showed tert-butyl radical to be nonplanar by 11°, with a barrier to inversion of 0.45 kcal/mol. It was noted that the inversion barrier may be the result of solvent stabilization of the dipole, which is nonzero only for nonplanar geometries. This effect, though, is likely to be too small to account for the observed barrier.

Electronegativity effects predict a tetrahedral structure for tert-butyl radical. In order to reconcile these arguments with experiment, it is necessary to assume that CH_3 is slightly less electronegative than carbon (12). Conjugative destabilization has also been suggested to induce nonplanarity in tert-butyl radical (8). Isotropic couplings of the trigonal carbon atoms with substituent groups were used to support these arguments. However, this model has recently been shown to be theoretically unsound (5). Investigations of the π interactions between the unpaired electron and substituent C–H orbitals in alkyl radicals have not yet been described.

There exists an additional effect that has not been considered in any of the above treatments. This is the direct, repulsive interaction between the bond pairs of the radical center and the bond pairs of adjacent alkyl substituents.[†] This interaction leads to an intimate coupling between the

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[†] This repulsive interaction is due to the requirement of orthogonality between bond pairs and is the cause of the rotational barrier of ethane and the staggered geometry of $C_2H_4^+$.

out-of-plane angle of the radical center and the torsional angle of the substituent methyl groups. The result is that for any one orientation of the substituents, out-of-plane bending of the radical center involves an unsymmetrical potential curve with a single minimum (usually at a nonplanar geometry). The combination of torsion and out-of-plane bending leads to a potential surface with multiple minima. The magnitude of the repulsive interactions relative to the inductive and conjugative effects discussed earlier will determine the nature of the barriers (if any) separating these minima, the degree of nonplanarity, and ease of deformation of the radical center. In the following discussion we present theoretical and experimental evidence for the importance of this interaction in determining the structure of alkyl radicals.

Recently, the results of several ab initio calculations have been reported on the ethyl radical (13, 14). Geometry variations using an STO-3G basis set (14) indicate that the CH_2 center is nonplanar and staggered with respect to the CH_3 group. The optimum planar geometry is eclipsed, and is calculated to be slightly above the staggered, nonplanar geometry. With the STO-3G basis, the separation between the staggered and planar geometries is 0.46 kcal/mol (14). This separation increases slightly to 0.62 kcal/mol with a 4-31G basis (14). More extensive calculations (13) (double zeta plus polarization basis) on the out-of-plane bending motion (maintaining a plane of symmetry) leads to a single minimum potential curve with an optimum angle of 6°. The separation between the planar and nonplanar geometries was found to be 0.2 kcal/mol. Similarly, STO-3G calculations on the tert-butyl radical indicate that the lowest energy C_{3h} conformation has a planar radical center (15), analogous to the eclipsed ethyl radical. When only C_3

symmetry is required, however, the calculations lead to a minimum energy structure involving a nonplanar radical center, with the CH_3 groups staggered with respect to the C–C bonds (12).

Although the absolute energy separations from all of these calculations may not be reliable, the trends are expected to be accurate. These trends indicate that alkyl radical centers are nonplanar and this nonplanarity is due to the direct repulsive interaction between the bond pairs around the radical center and those of adjacent substituents. It is to be expected, therefore, that pyramidal radical centers and preferred orientations of substituent groups will be linked. When this preference becomes sufficiently strong, a barrier to internal rotation will be evident in ESR experiments.[‡]

Further evidence for the link between pyramidal radical centers and barriers to internal rotation has been found in studies of halogenated radicals. For example, α-substitution of two fluorine atoms in ethyl radical induces a strongly pyramidal radical center and an observable barrier to internal rotation (16). Steric interactions and special H-F interactions were ruled out as being the cause of the barrier. It was concluded that the strength of the nonplanarity of the radical center controlled the height of the

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[‡] As an example of a multiple minimum potential with no experimentally observable barriers, consider the ethyl radical. Allowing both torsional motion and inversion about the radical center, a total of six equivalent, nonplanar, staggered structures are generated. The calculations indicate that the lowest energy pathway between any two of these will be a combined torsion and inversion involving a planar or nearly planar radical center. The barriers involved are too small to hinder motion except at extremely low temperatures. Hence, the radical appears to have free internal rotation in ESR experiments (6).

barrier, and furthermore that two α-fluorine substituents were necessary to produce an observable effect. In addition, matrix studies of β-halo tert-butyl radicals indicate that these species have preferred orientations relative to the center carbon and the two other methyl groups (17). It has been suggested that nonplanarity at the radical site enhances the relative stability of these staggered forms. This coupling of the out-of-plane angle and internal rotation was also proposed to be the source of the negative temperature dependence of the halogen hyperfine splitting constant.

In summary, theoretical calculations indicate that the out-of-plane bending potentials of alkyl-substituted radicals are highly asymmetric and involve a single nonplanar minimum. It is suggested that the origin of this effect lies in the orthogonality-induced bond-pair repulsions analogous to those leading to hindered internal rotations in alkanes. This effect leads not only to nonplanar equilibrium geometries for the alkyl radicals, but also to a strong coupling between the torsional and out-of-plane bending modes in these systems. Experimentally, barriers to internal rotation of 2.5 kcal/mol or more are necessary to produce an observable effect in ESR spectra. Inversion doubling requires barriers in excess of 5 kcal/mol to produce an observable effect. Theoretical calculations predict that the corresponding barriers in the alkyl radicals are on the order of 0.5 kcal/mol or less, and should not be easily observed. In fact, this has been found to be the case. Their ESR spectra are characteristic of essentially free internal rotation, and evidence has been found mainly in the form of anomalous temperature dependences in tert-butyl radical. It has been suggested[§] that, in order for the

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[§] Griller, D. and Preston, K. F., submitted for publication.

effect of coupled torsions and out-of-plane bends to be observed in ESR, the energies of the two modes must be comparable. As discussed elsewhere,[¶] photoelectron experiments have also been cited as evidence for the non-planarity of the alkyl radicals, however, just how much of the geometry change incurred on ionization is due to the out-of-plane conformation remains an open question.

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[¶] Houle, F. A., and Beauchamp, J.L., to be submitted.

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CHAPTER IV

Photoelectron Spectra of Secondary Cyclic Radicals. Implications for the Structure and Stability of Cyclopentyl, Cyclohexyl and 2-Norbornyl Cations in the Gas Phase

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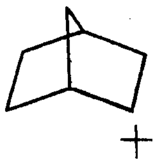
Abstract

The first photoelectron band of 2-norbornyl radical has been obtained, together with those of cyclopentyl and cyclohexyl radicals which serve as models for the bicyclic species. The adiabatic and vertical ionization potentials for 2-norbornyl and 2-norbornyl-2-*d* radicals coincide, and are 6.84 ± 0.02 and 6.83 ± 0.02 eV, respectively. The monocyclic radicals, on the other hand, have broad, featureless bands. Adiabatic and vertical ionization potentials, respectively, are determined to be 7.21 ± 0.02 and 7.46 ± 0.02 eV for cyclopentyl radical, and 7.15 ± 0.04 and 7.40 ± 0.04 eV for cyclohexyl radical. The data are used to characterize the stabilities of 2-norbornyl radical and cation in comparison to other secondary species. Although it is not possible to interpret the Franck-Condon envelope fully due to experimental difficulties, it may be inferred from the spectrum that the lowest energy structure of 2-norbornyl cation does not differ significantly from that of the radical in the gas phase. Thermal decomposition of 2-norbornyl radical has been observed in these experiments, and a mechanism consistent with products identified in the photoelectron spectra is proposed.

Introduction

Organic ions having several degenerate or nearly isoenergetic configurations connected by relatively low barriers will be characterized even at low temperatures by a rapid equilibrium among the structures. Conventional spectroscopic studies (e.g., magnetic resonance) of these ions will generally give information on an "averaged" structure rather than the minimum energy configurations themselves because the intrinsic experimental time scales are long compared to the equilibration rate. An alternative approach to obtaining information relating to the structure and stability of organic ions is to examine the photoelectron spectra of the corresponding radicals. The ionization process, which occurs in 10^{-16} sec, effectively takes a "snapshot" of the ion from the point of view of the radical. In analogy with electronic spectroscopy, if the ion and radical have nearly identical lowest-energy structures, then the spectrum will be sharp. Large geometry differences, on the other hand, will be reflected in broad photoelectron bands. In favorable cases, the Franck-Condon envelope of the band can be analyzed to obtain quantitative information regarding structural changes incurred on ionization.

2-Norbornyl cation is a species that is thought[1] to have equilibrating classical (1) or σ-bridged (2) structures. It is these two



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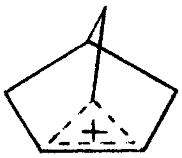

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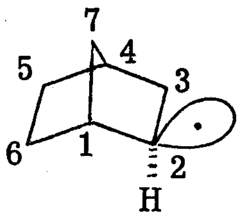

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structures that are compared to that of the radical (3) in the photoelectron spectrum. Although there are essentially no gas phase data on 2-norbornyl radical, studies in condensed phase are expected to provide useful information since solvent-radical interactions are relatively weak. These studies fall into two groups: electron spin resonance experiments (ESR) and stereoselectivity of reagent attack on the radical.

The rigidity of 2-norbornyl radical has allowed rather detailed analyses of its structure to be performed using hyperfine interactions determined by ESR. The radical has been found[2, 3] to have inequivalent protons at the 3-position, and unusually strong γ (6-position) hyperfine couplings. It was concluded that the unpaired electron enjoyed enhanced delocalization compared to acyclic and monocyclic hydrocarbon radicals. Indeed, the spin density at the radical center was estimated[2] to be 0.70, compared to 0.84 for isopropyl radical[4] and 0.78 for tert-butyl radical.[4] It was also concluded that the inequivalent β-couplings could arise from either a planar radical whose skeleton has been slightly twisted about the C_1-C_4 axis[2] or an undistorted radical with a nonplanar trigonal center.[3] Subsequently, support for the latter interpretation was found in a study of the effect on β-couplings of substitution of electronegative groups at the 3-position.[5] The observed ESR spectra were found to be consistent with 2-norbornyl radicals having C_2-H bonds bent in the endo direction at an angle dependent on the nature of the substituent. In the case of 2-norbornyl itself, this angle has been estimated to be 20-30°.[3] Further support for the endo configuration of the C_2-H bond is given by the existence of long-range hyperfine couplings,[6] the magnitude of which have been shown to be critically dependent on the configuration at the radical center.[7]

Studies of the kinetics and stereochemistry of atom abstraction reactions of 2-norbornyl radical with various atom donors in solution provide additional information on its properties.[8] The proposed structure 3 is consistent with the observed chemistry of 2-norbornyl radical. H and Cl atom-transfer reactions at the *exo* position were moderately favored over reaction at the *endo* position. This selectivity was found to depend on the nature of the atom donor. It was concluded that the observed effects could be rationalized on the basis of steric factors, including hindrance to motion of the C_2-H bond towards the *exo* position on reagent attack from the *endo* side.

No experimental information is available for the structure of 2-norbornyl cation in the gas phase. Experiments in condensed superacid media,[9, 10] however, have provided evidence that 2 is more appropriate than 1. ESCA spectra of the cation[9] were found to be consistent with two types of carbons having a ratio of 2:5, where 1:6 would have been expected for a purely classical structure 1. In addition, the range of C(1s) binding energies observed was much smaller than that expected for a classical ion. This interpretation is supported by calculations of core-hole state spectra at the 4-31G level.[11] More recently, studies of isotopic perturbation of NMR chemical shifts[10] have been interpreted in terms of symmetrically bridged structure 2 for 2-norbornyl cation.

Theoretical calculations[12, 13] have been performed in order to determine the difference in energy between 1 and 2. Since the results pertain to an isolated ion, they are expected to be relevant to gas-phase systems. Calculations for the two structures were performed using *ab initio*[12] and semi-empirical[13] methods. Geometries were optimized in both studies, and were found to be strongly dependent on the calculational approach used. Charge distributions were also found to differ significantly. Nevertheless, both methods predicted 1 to be the most stable form of the ion by 5.2 kcal/mol[12] (STO-3G basis set), 0.2 kcal/mol[12] (STO4-31G basis set) and 1.9 kcal/mol[13] (MINDO/3). It was suggested[12] that a larger basis set and inclusion of correlation effects would preferentially lower the energy of 2, making it the most stable form. It is only possible to conclude from these calculations that the two structures 1 and 2 are likely to be close in energy.

Consideration of the theoretical results for the ion and the experimental data for the radical allows two qualitatively different predictions to be made for the first photoelectron band of 2-norbornyl radical. (It is assumed that formation of 1 from the radical will require little or no structural rearrangement, while formation of 2 will involve substantial changes. The presence or absence of such changes will be reflected in the width or narrowness, respectively, of the Franck-Condon envelope of the photoelectron band.) The two possibilities are: (a) formation of a classical ion only, with evidence for little or no geometry change because of the rigidity of the carbon framework; or (b) formation of a nonclassical ion only, with a broad Franck-Condon envelope, and excitation of many vibrational degrees of freedom.

In addition to obtaining information on the structure of 2-norbornyl cation in the gas phase, a goal of these experiments was to determine the ionization potential (IP) of 2-norbornyl radical and use it to characterize the thermochemistry of the radical-ion system. While measures of the heat of formation of the ion are available,[14-16] none have been made of the radical. An estimate of its heat of formation and the homolytic bond energy in norbornane can be made, however, by combining the heat of formation of the ion with the IP of the radical. Also presented in this work are photoelectron spectra for cyclohexyl and cyclopentyl radicals. The purpose of obtaining these was to provide data for other large secondary ions to compare to those for 2-norbornyl cation, using various criteria for assessing ion stability.

Experimental Section

The photoelectron spectrometer used in these experiments is of standard design, comprising a capillary discharge lamp, a 127° electrostatic analyzer, and a Channeltron electron multiplier. It has been specifically modified to study the products of pyrolysis. A more detailed description has been given elsewhere.[17]

All radicals were produced by pyrolysis of the alkyl nitrites, according to the reactions

$$\begin{aligned} \mathrm{RCH_2ONO} &\rightarrow \mathrm{RCH_2O\cdot} + \mathrm{NO} \\ \mathrm{RCH_2O} &\rightarrow \mathrm{R\cdot} + \mathrm{NO} \end{aligned} \tag{1}$$

where R = 2-norbornyl, 2-norbornyl-2-*d*, cyclopentyl and cyclohexyl.

The nitrites were prepared from the corresponding alcohols using one of two standard techniques.[18, 19] Cyclopentanemethanol and cyclohexanemethanol were obtained from Aldrich. Labelled and unlabelled exo- and endo-bicyclo [2. 2. 1] heptan-2-methanol were synthesized using literature methods.[20]

Pyrolysis spectra were recorded over a temperature range of 385°-685° C, using a mixture of exo- and endo-bicyclo [2. 2. 1] heptan-2-methyl nitrite, pure exo-nitrite, pure endo-nitrite, a mixture of exo- and endo-bicyclo [2. 2. 1] heptan-2-methyl nitrite-2-d, and cyclopentyl and cyclohexyl methyl nitrite. Good yields (~15-20 counts per second for 2-norbornyl radical, 10 cps for cyclopentyl radical, and 5 cps for cyclohexyl radical) of the radicals were only obtained at the lower end of the temperature range because the radicals themselves decompose under the same conditions as their nitrite precursors. Mechanisms for cyclohexyl and cyclopentyl radical thermolysis are described elsewhere,[21] that for 2-norbornyl radical is discussed in the results section. Both HeI and NeI radiation were used in these experiments. Energy scales were calibrated using both α and β bands of CH_2O, NO and Ar. The resolution was approximately 30-35 mV for these experiments, and a reasonable estimate of our error is ± 0. 02 eV for all radicals except cyclohexyl radical, which is ± 0. 04 eV.

Results

Spectra obtained in these experiments are presented in Figures 1-5 and 7-9. The data for the individual radicals will be discussed in this section, and compared to previous work where possible.

Nitrites. The photoelectron spectra of exo- and endo-bicyclo[2.2.1] heptan-2-methyl nitrite were superimposible, and a spectrum of a mixture of the two isomers is shown in Figure 1. Spectra for cyclopentyl and cyclohexyl methyl nitrite are presented in Figures 2 and 3, respectively. The vertical IPs of these species are approximately 10.3, 10.4 and 10.3 eV, respectively.

2-Norbornyl Radical. Representative spectra of 2-norbornyl radical are presented in Figure 4. Figures 4a and 4b show bands recorded at the lowest temperature at which the radical could still be detected, while Figure 4c shows a higher temperature spectrum. It can be seen that it differs in the region following the sharp feature at ~ 6.8 eV in that a new band appears to be growing in, having a maximum at ~ 7.0 eV. At higher temperatures (~600° C), the sharp band diminishes even further with respect to the 7.0 eV feature, and finally, on reaching 650-700° C both bands essentially disappear. Throughout this sequence of events, bands attributable to cyclopentadiene[22] and ethyl radical[23] (which are the only major new pyrolysis products) become progressively more prominent in the spectrum. While barely present in Figure 5a, they are both readily identifiable in Figure 5b. These observations are corroborated by recent mass spectrometric experiments by F. P. Lossing.[24, 25]

The thermal decomposition mechanism of 2-norbornyl radical, which does not appear to have been investigated previously, can be deduced as follows. In general, hydrocarbon radicals undergo two major types of unimolecular reactions, to the exclusion of almost all

FIGURE 1

HeI photoelectron spectrum of a mixture of <u>exo</u>- and <u>endo</u>-bicyclo[2. 2. 1]heptan-2-methyl nitrite.

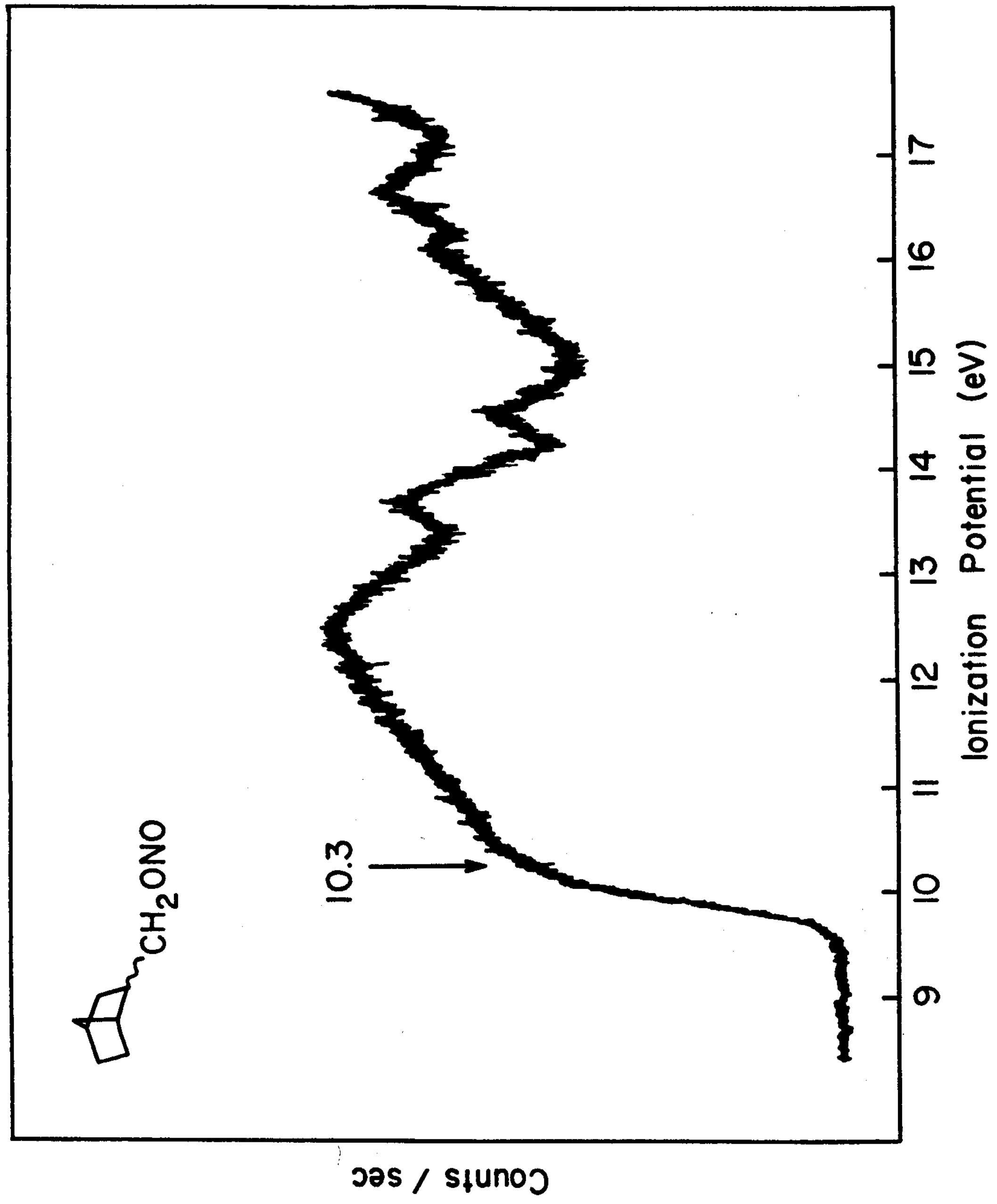
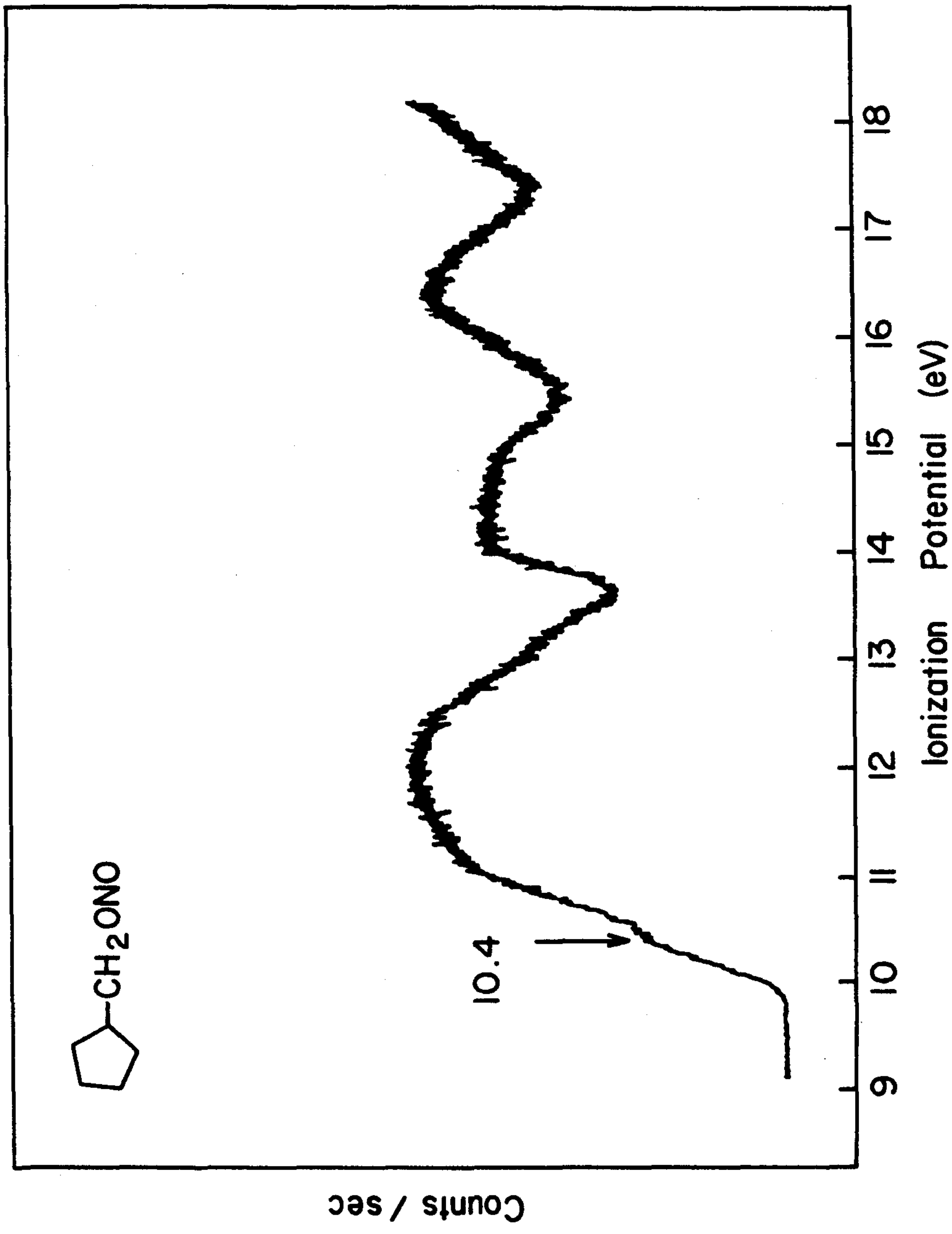

CH$_2$ONO
10.3
9
10
11
12
13
14
15
16
17
Ionization Potential (eV)
Counts / sec

FIGURE 2

HeI photoelectron spectrum of cyclopentyl methyl nitrite.



CH2ONO
10.4
9
10
11
12
13
14
15
16
17
18
Ionization Potential (eV)
Counts / sec

FIGURE 3

HeI photoelectron spectrum of cyclohexyl methyl nitrite.

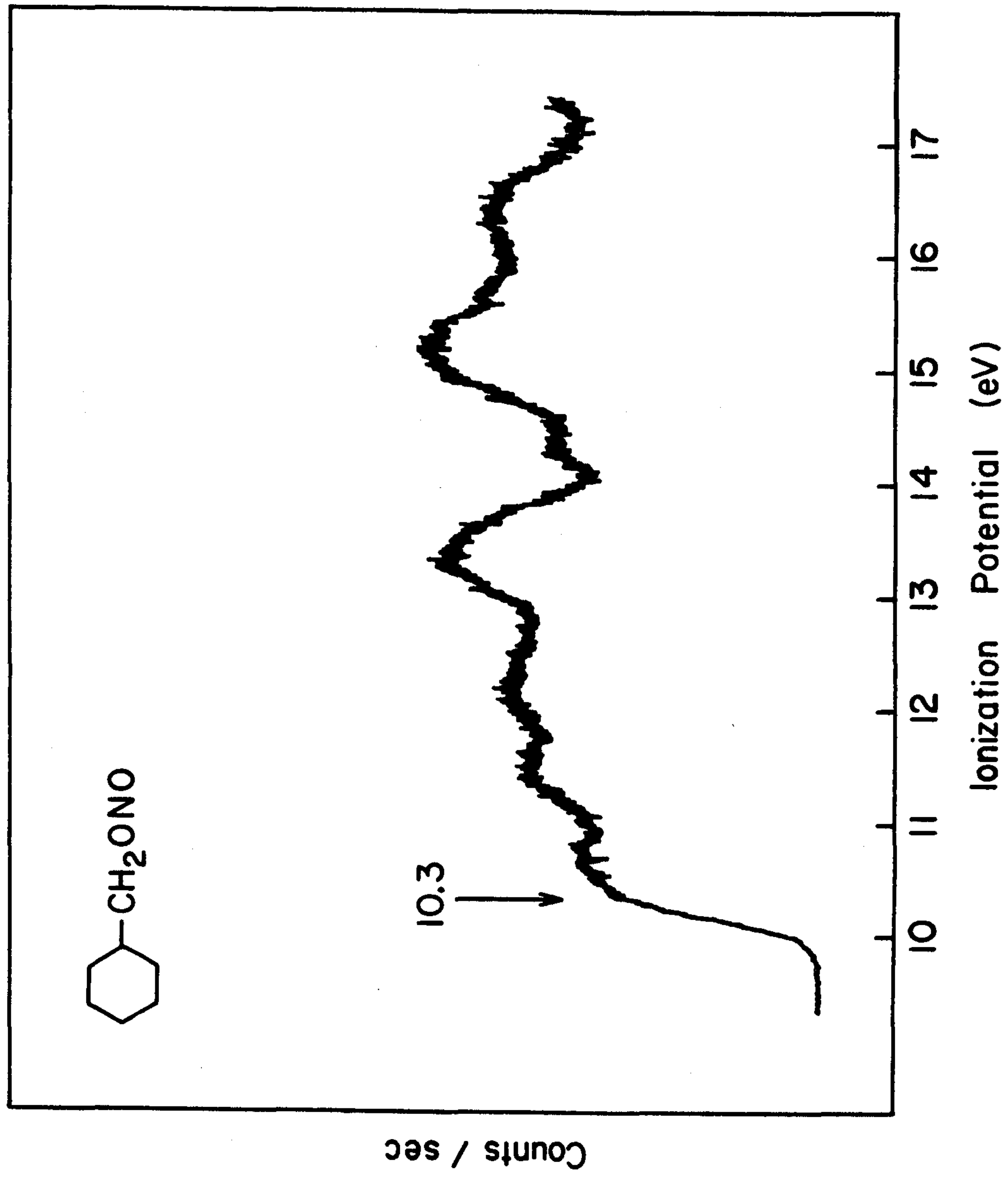

CH₂ONO
10.3
10
11
12
13
14
15
16
17
Ionization Potential (eV)
Counts / sec

FIGURE 4

First photoelectron band of 2-norbornyl radical, recorded with HeI radiation.

(a) Generated from pure exo-bicyclo[2. 2. 1]heptan-2-methyl nitrite at 401°.

(b) Generated from exo- and endo-bicyclo[2. 2. 1]heptan-2-methyl nitrite at 404°.

(c) Generated from the same starting material as (b), but at 582° C.

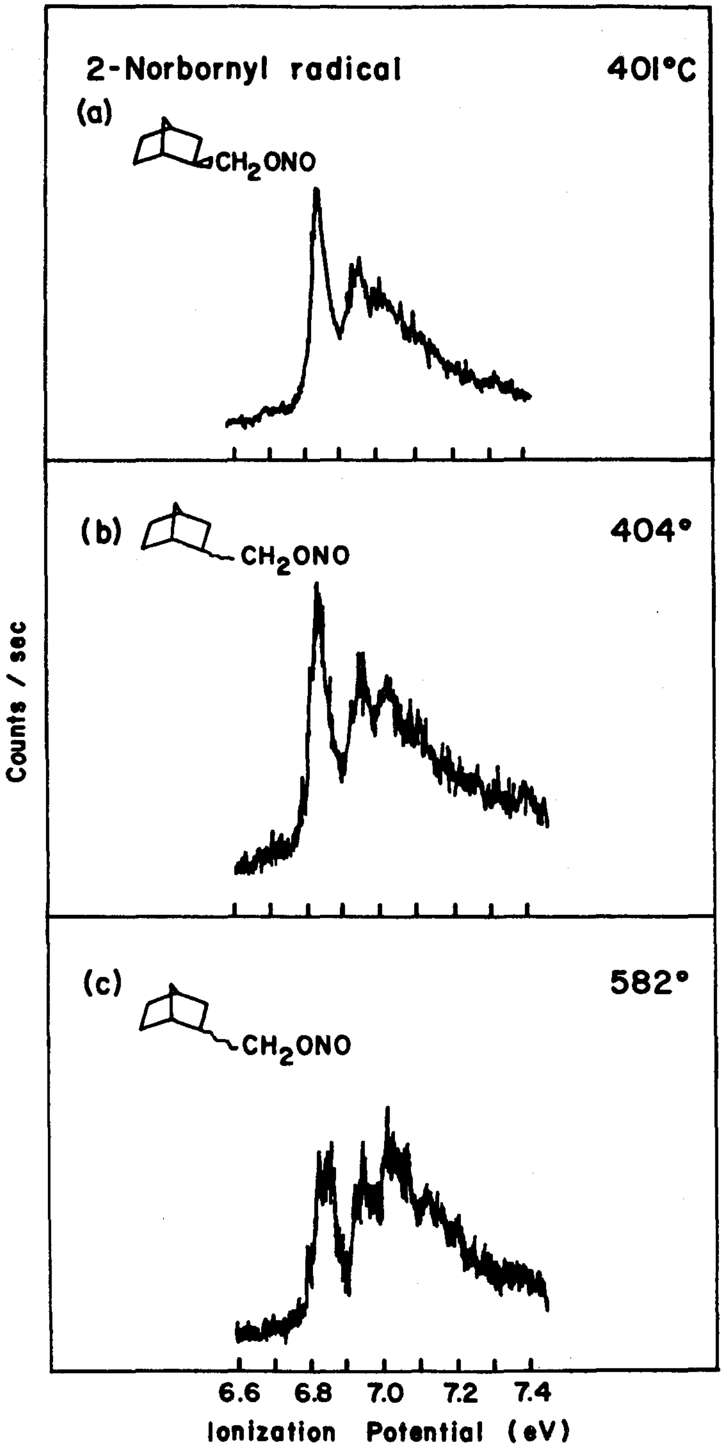
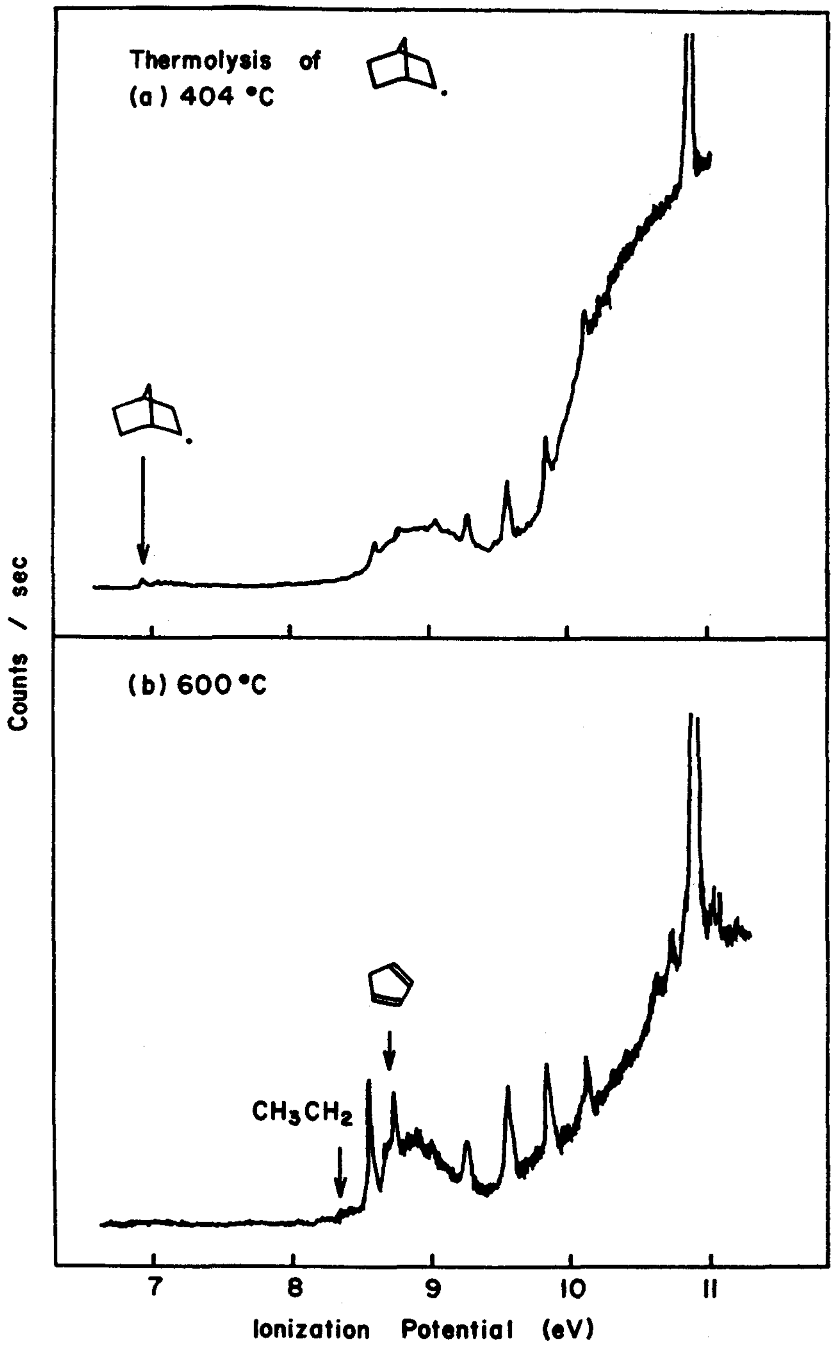

2-Norbornyl radical
401°C
(a)
CH$_2$ONO
(b)
CH$_2$ONO
404°
(c)
CH$_2$ONO
582°
Counts / sec
6.6
6.8
7.0
7.2
7.4
Ionization Potential (eV)

FIGURE 5

Major thermolysis products of 2-norbornyl radical. The bands at 10. 884 and 9. 26-10 eV are from CH_2O and NO, respectively.

(a) Spectrum at 404° C.

(b) Spectrum at 600° C.


Thermolysis of
(a) 404 °C
(b) 600 °C
CH_3CH_2
Counts / sec
7
8
9
10
11
Ionization Potential (eV)

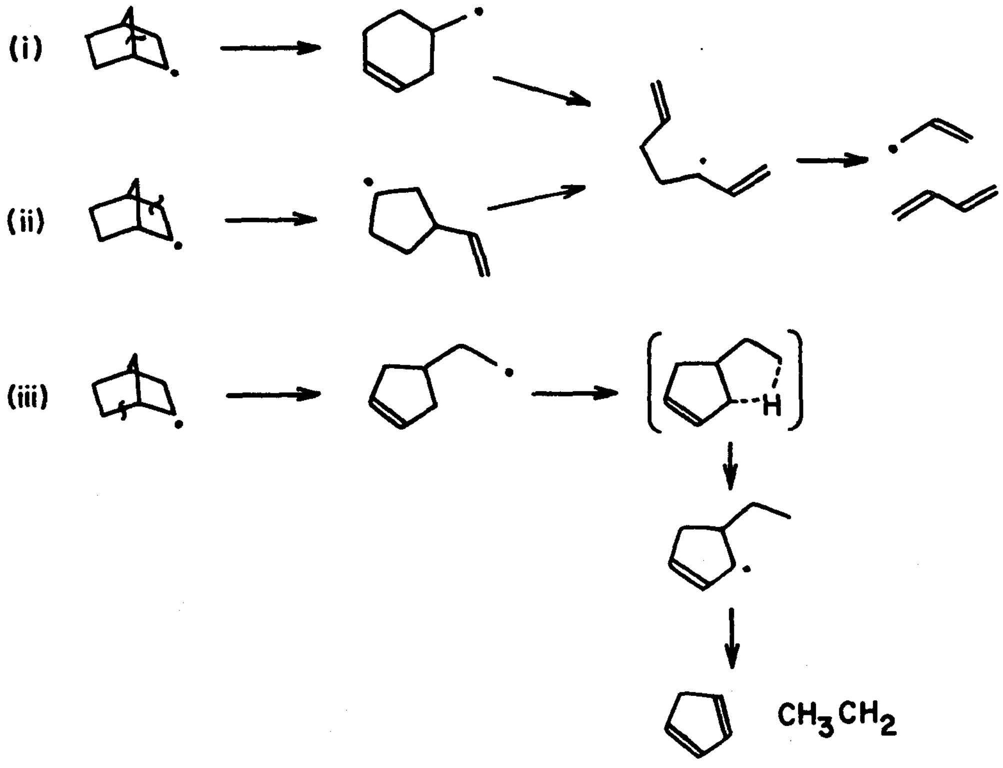
others: scission of the C–C bond β to the radical center, and loss of a β-H.[26] 2-Norbornyl radical has three C–C β to the 2-position: the three resulting reaction pathways are shown in Figure 6. Loss of H to form norbornene may also occur, however, large contributions from it and its thermolysis product C_2H_4 are not evident in the photoelectron spectra recorded at higher temperatures. Apparently the relative rate of C–C cleavage is very much higher in this system. Pathways i and ii both give rise to allyl radical[17] and butadiene,[27] neither of which is found in Figure 5. The products from pathway iii, however, are both found in Figure 5, indicating that it is the main mode for decomposition of 2-norbornyl radical under low pressure, fast flow conditions. The primary radical initially formed in iii is assumed to undergo a 1, 4 H shift to form the more stable ethylcyclopentenyl radical.[24] Precedent for such a rearrangement in the PES is found in the cyclohexyl radical decomposition.[21] The parent cyclopentenyl radical has an IP of 7. 00 eV,[28] as determined by electron impact. Thermochemical estimates[29] taken together with the hydride affinity calculated for cyclopentenyl cation[28] indicate that the ethyl substituent on the five-membered ring should not affect the IP very much. Thus, it is possible that the new feature found in Figure 4c at 7. 0 eV may arise from the intermediate ethylcyclopentenyl radical.

This mechanism can be compared to the results of the pyrolysis of 1, 7, 7-trimethyl[2. 2. 1]bicyclohept-2-yl radical at 255-290°C in the gas phase.[30] The pathways analogous to ii and iii for the parent 2-norbornyl radical were observed, while that similar to i had not yet

FIGURE 6

Schematic of major C–C cleavage reactions which can occur in 2-norbornyl radical thermolysis.

Possible Decomposition Pathways of 2-Norbornyl-Radical



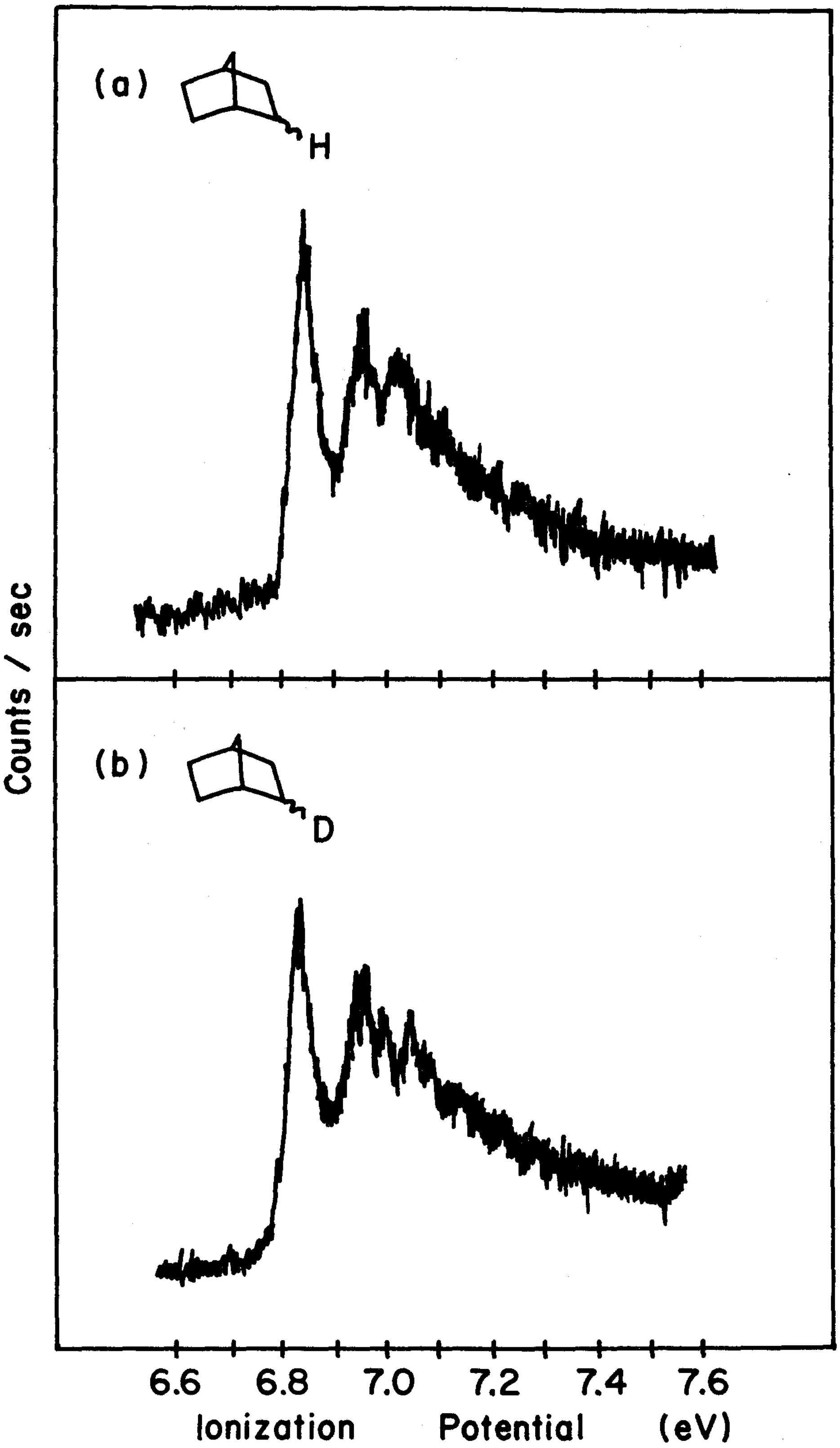
been identified. Although no details were given, it appears that the pressure regime was much higher than that for the present work, since comparatively few of the bicyclic radicals rearranged or fragmented prior to scavenging. It is not possible to compare the relative importance of ii and iii in the substituted system to that found for 2-norbornyl radical. This is because the pathway analogous to ii involves ring-opening to a tertiary radical rather than a primary one, and is likely to be favored.

Spectra of 2-norbornyl radical obtained from both the exo- and endo-nitrites, or a mixture of the two, were indistinguishable and highly reproducible, as shown in Figures 4a and 4b. Moreover, as seen in Figure 7, deuterium labelling at the 2-position did not affect any of the spacings within the photoelectron band, but did yield a shift in the IP, the amount and direction of which are typical for saturated alkyl radicals.[23] The latter result provides evidence that the sharp feature (at least) arises from ionization of a species labelled with deuterium at its radical site, and this is most likely to be an unrearranged 2-norbornyl radical. Further evidence for the correctness of this assignment is given by the fact that the measured IP is consistent with independent energetics data for 2-norbornyl cation in the gas phase. This point will be examined in detail in the discussion section.

On the basis of the experiments discussed in the preceding paragraphs, only the first sharp peak in Figures 4a, 4b and 7 can be taken to arise unambiguously from 2-norbornyl radical. These features

FIGURE 7

First photoelectron band of (a) 2-norbornyl radical and (b) 2-norbornyl-2-*d* radical, both recorded at 404° C.


(a)
H
(b)
D
Counts / sec
6.6
6.8
7.0
7.2
7.4
7.6
Ionization Potential (eV)

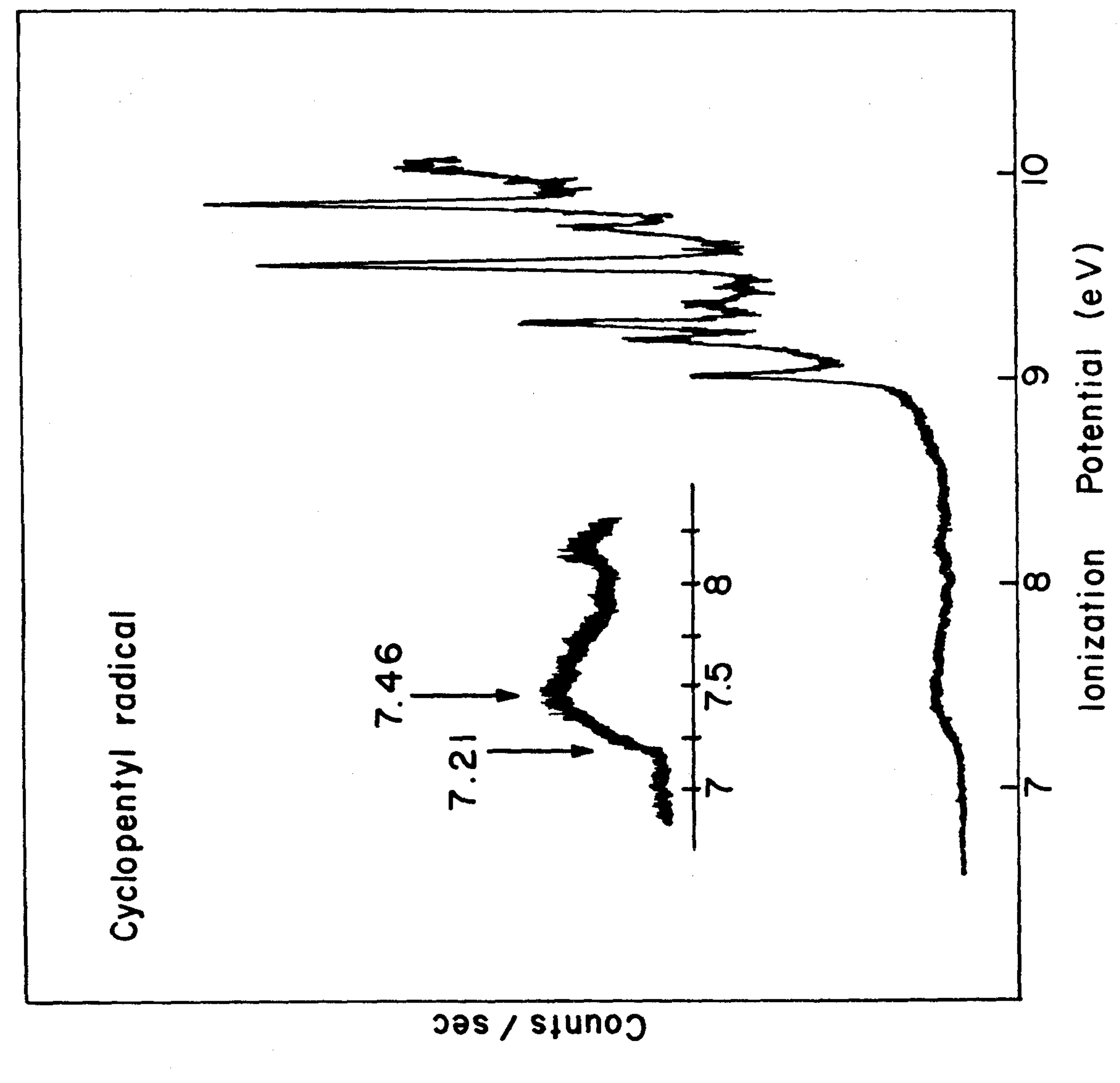
are not only the lowest energy ones in the band, but also the most intense. Therefore, the adiabatic and vertical IP for 2-norbornyl radical is determined to be 6.84 ± 0.02 eV, and that for 2-norbornyl-2-*d* radical is 6.83 ± 0.02 eV.[31] This is the first experimental measurement of the ionization energy of these species. Comparison of Figures 4a, 4b and 4c suggests also that the feature at 6.97 eV is associated with the lowest energy peak. If these two features are members of a vibrational progression, their spacing gives a frequency of $\sim$1050 cm^{-1} in the ion.

The coincidence of vertical and adiabatic IPs for 2-norbornyl radical indicates that the nuclear coordinates do not differ appreciably between it and 2-norbornyl cation. However, ionization is probably accompanied by changes in force constants, as evidenced by the observed isotope effect on the IP.[32] The extent to which these changes occur could be gauged qualitatively from the breadth of the photoelectron band, if the composition of the band were accurately known. Unfortunately, even data taken at the lowest temperatures (Figures 4a, 4b and 7) may reflect a substantial contribution from secondary reaction products.

Cyclopentyl Radical. The first photoelectron band of cyclopentyl radical, recorded with NeI light, is shown in Figure 8. The band was found to be smooth and featureless. The present experiments give adiabatic and vertical IPs of 7.21 ± 0.02 and 7.46 ± 0.02 eV, respectively, for cyclopentyl radicals. There have been two previous determinations using electron impact ionization: 7.79 ± 0.03[33] and

FIGURE 8

Photoelectron spectrum of cyclopentyl radical by NeI radiation. The features at 9. 2-10 and 10. 884 eV are from NO and CH_2O, respectively.


Cyclopentyl radical
7.46
7.21
7
7.5
8
7
8
9
10
Ionization Potential (eV)
Counts / sec

7.47 ± 0.05[34] eV. The second of these, which involved a high resolution electron beam, is in good agreement with the vertical IP reported here.

Cyclohexyl Radical. In Figure 9 is presented the first photoelectron band of cyclohexyl radical, recorded using NeI radiation. The band is smooth and featureless, like that of cyclopentyl radical. Poor signal to noise made accurate determination of both the band onset and maximum extremely difficult, so large error bars are assigned to these measurements. The adiabatic and vertical IPs are determined to be 7.15 ± 0.04 and 7.40 ± 0.04 eV, respectively. The only previous measurement of the IP of cyclohexyl radical is 7.66 ± 0.05 eV,[33] somewhat higher than the values reported here.

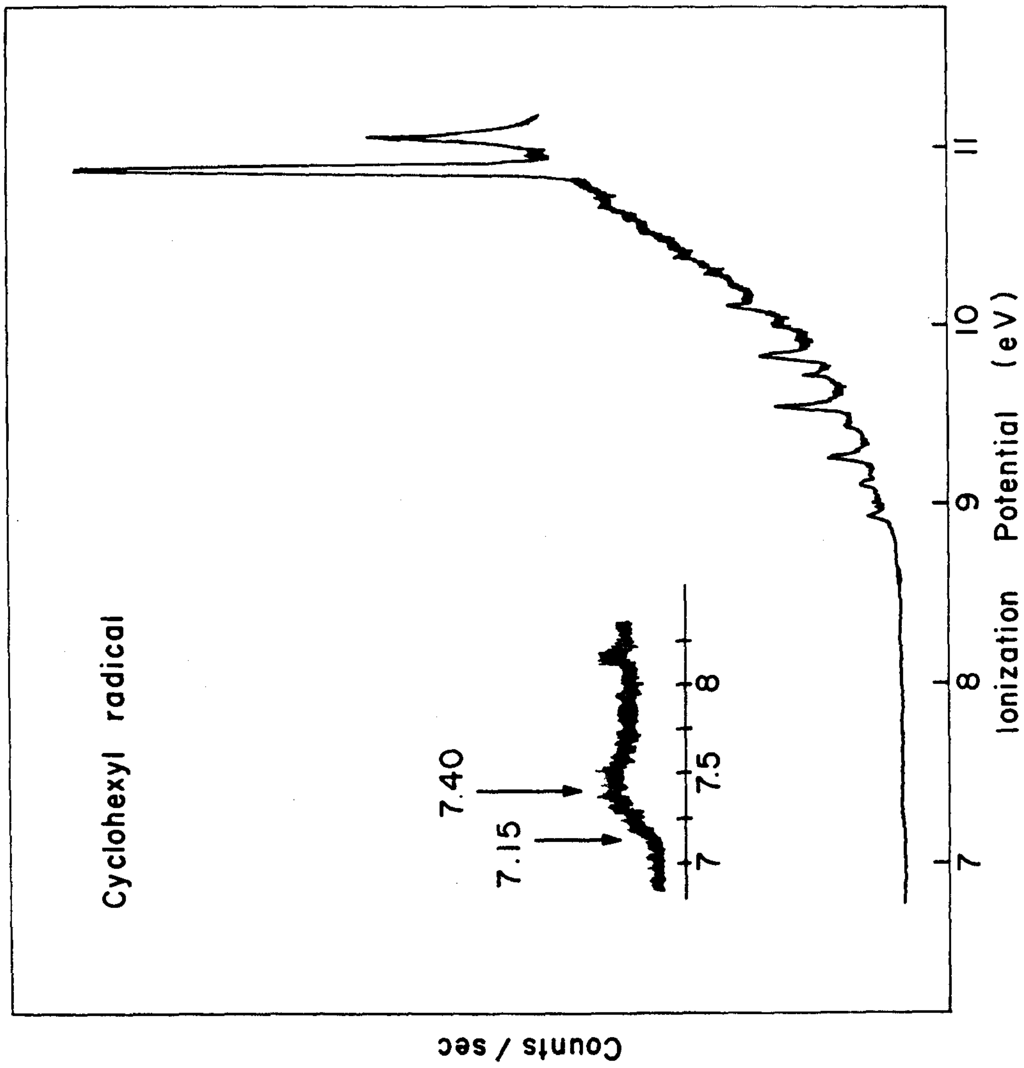
Discussion

Because the most important features of the 2-norbornyl radical photoelectron spectrum can be identified, the experimental difficulties noted in the results section should not completely prevent interpretation of the data. Indeed, the ionization potentials can be used to characterize the stability of both cation and radical both in absolute terms and in comparison to the two model systems. In addition, one possible gas phase structure for 2-norbornyl cation can be ruled out on the basis of the present results. The more difficult task of deciding what the ion *does* look like, however, must await a full understanding of the details of the photoelectron band.

Energetics of Radicals and Cations. The simplest secondary free radical, isopropyl radical, has an adiabatic ionization potential of

FIGURE 9

NeI photoelectron spectrum of cyclohexyl radical. The features at 9. 2-10 and 10. 884 eV are from NO and CH_2O, respectively.


Cyclohexyl radical
7.15
7.40
7
7.5
8
7
8
9
10
11
Ionization Potential (eV)
Counts / sec

7.36 eV.[23] Increasing the size of the molecule, and cyclizing it does not cause this value to be lowered very much: cyclopentyl radical has an IP of 7.21 eV, and cyclohexyl radical 7.15 eV. The effect is approximately 0.07 eV per additional carbon. On the basis of this, an IP for 2-norbornyl radical, a C_7 species, would be predicted to be ~ 7.08 eV. This is substantially higher than the value actually measured, 6.84 eV, which is actually closer to the adiabatic IP of tert-butyl radical, 6.70 eV. The unusually low value for the IP of 2-norbornyl radical indicates that either the unpaired electron in the radical is much higher in energy than in other secondary radicals, or the carbonium ion is much more stable than other secondary ions. These alternatives, while highly simplified, will be useful in discussing the origin of the remarkably low ionization energy. Before examining this further, however, it is necessary to obtain relevant thermochemical parameters from available experimental data on 2-norbornyl cation.

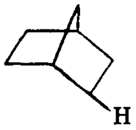
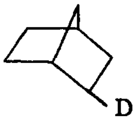
The gas phase proton affinity (PA) of norbornene has been determined to be 3.5 kcal/mol lower than that of ammonia.[14] PA(NH_3) has recently been reevaluated on the basis of more accurate data for reference standards in the proton affinity scale,[23] and is found to be 208.4 kcal/mol. Thus, if the proton affinity of norbornene is 204.9 kcal/mol, the heat of formation of 2-norbornyl cation can be calculated to be 181.9 kcal/mol, as listed in Table I. This is in good agreement with the values of 181.1[15] and 182.3[16] kcal/mol resulting from hydride transfer[15, 16] and proton transfer[16] equilibrium studies. Combining

ΔH_f (2-norbornyl$^+$) = 181.9 kcal/mol with the IP of the radical, the heat of formation of the radical is calculated to be 24.2 kcal/mol. No previous experimental determinations of this quantity could be found in the literature. The heat of formation of the cation can also be used to calculate the heterolytic bond dissociation energy in norbornane, 229.0 kcal/mol.

The question of the stabilities of 2-norbornyl radical relative to other secondary radicals and of 2-norbornyl cation relative to other secondary cations can now be considered. A convenient measure of relative stabilities of radicals and cations is found in homolytic and heterolytic bond dissociation energies, respectively, which are listed in Table I.

Norbornane is calculated to have a homolytic bond dissociation energy at the 2-position of 88.7 ± 3 kcal/mol, where the two largest sources of error are the relative proton affinity of norbornene[14] and the absolute proton affinity of ammonia.[23] This value is substantially lower than that for propane at the 2-position, but only slightly lower than those of cyclopentane and cyclohexane, which have errors of at least ± 3 kcal/mol.[37] An alternate route can be used to calculate the homolytic bond energy in cyclopentane, independent of any measured or assumed value for the heat of formation of cyclopentyl radical, in order to test the accuracy of the data used in Table I. Hydride transfer equilibria have been observed between isopropyl cation and cyclopentane.[15, 16] The enthalpy associated with this process was measured to be -5.9 kcal/mol. This value gives a heat of formation for

Table I. Thermochemical Data for 2-Norbornyl and Related Systems[a]

R	$\Delta H_f(R\cdot)$	IP(R)		D(R-H)	$\Delta H_f(R^+)$[b]	$D(R^+H^-)$[b]	PA(alkene)[b]
		Adiabatic	Vertical				
CH_3CHCH_3	17.6[c, d]	7.36[e]	7.69[e]	94.5	187.3	246.8	183.3
	22[c]	7.21	7.46	92.5	188.2	241.4	185.7
	12[c]	7.15	7.40	93.6	176.9	241.4	187.7
	24.2[f]	6.84	6.84	88.7[f, g]	181.9[f, h]	229.0[f, g]	204.9[i]
	--	6.83	6.83	--	--	--	--
$C(CH_3)_3$	8.4[d]	6.70[e]	6.92[e]	92.9	162.9	230.0	198.5

[a] All IPs in eV, all other quantities in kcal/mol at 298°K. Error limits for IPs are ± 0.02 eV except cyclohexyl radical (± 0.04 eV) and tert-butyl radical (± 0.03 eV). All other error limits ± 1-3 kcal/mol. Data are consistent with $PA(NH_3)$ = 208.4 kcal/mol (Ref. 23).

[b] All heats of formation are calculated using the convention that the heat of formation of an electron at rest is zero at all temperatures. Accordingly, the following values are used: $\Delta H_f(H^+)$ = 365.7 kcal/mol, and $\Delta H_f(H^-)$ = 34.7 kcal/mol (Ref. 35). Heats of formation of alkanes and alkenes are taken from Ref. 36, except for the norbornyl system.

[c] Ref. 36

[d] Ref. 37.

[e] Ref. 23.

[f] Calculated using data in this table.

[g] ΔH_f(norbornane) = 12.42 kcal/mol (Ref. 38).

[h] ΔH_f(norbornene) = 21.12 kcal/mol (Ref. 39).

[i] Ref. 14.

cyclopentyl cation of 187.9 kcal/mol. Combining this with an adiabatic IP of 7.21 eV for cyclopentyl radical, a heat of formation of 21.6 kcal/mol is obtained for the radical. This new value is in excellent agreement with that of Kerr,[37] lending support to a homolytic bond energy of 92.5 ± 3 kcal/mol for that species.

These considerations lead to the conclusion that norbornane has a slightly lower C–H bond dissociation energy than cyclopentane and cyclohexane, and thus that 2-norbornyl radical is somewhat more stable than either monocyclic radical. This is consistent with ESR results[2, 3] described in the introduction, which showed that H_γ hyperfine couplings were unusually large in 2-norbornyl radical. In both studies, the conclusion was drawn that unpaired spin was very effectively delocalized in this species, compared to both mono-cyclic and acyclic carbon-centered radicals.[4] This delocalization provides a means for enhancement of the stability of 2-norbornyl radical over that which is normally expected for secondary radicals.

In view of this result, the exceptionally low IP of 2-norbornyl radical must reflect enhanced stability for both radical and cation. Further indication that this is the case for the positive ion is found in the comparison of heterolytic bond dissociation energies for norbornane and other cyclic alkanes.

Recent studies of hydride transfer equilibria between tertiary alkyl ions in the gas phase[40] showed that values measured for heterolytic bond dissociation energies of these species were almost independent of the size of the ion once it exceeded five carbons, reaching a limiting value of ~ 224 kcal/mol. Using data available in the literature, it was argued that secondary ions would show similar behavior, the limiting value for the hydride affinity being ~ 241 kcal/mol. The data shown in Table I for isopropyl, cyclopentyl and cyclohexyl cations are in good agreement with this, and lead to the prediction that 2-norbornyl cation should have a hydride affinity of 241 kcal/mol. It can be seen that the actual value is 12 kcal/mol lower than this. Thus, 2-norbornyl cation is exceptionally stable compared to other secondary cations, but still 5 kcal/mol less than the expected stability for 2-methyl-2-norbornyl cation, assuming that the latter is a normal tertiary ion. Experimentally,[15] 2-methyl-2-norbornyl cation has been found to be 6 ± 2 kcal/mol more stable than 2-norbornyl cation, in good agreement with the estimated value.

These gas-phase results are consistent with calorimetric studies of ionization processes in solution.[41, 42] The general reaction studied is

$$\mathrm{RCl} + \mathrm{SbF_5} \xrightarrow[\Delta H_i]{} \mathrm{R^+[Sb_xF_{5x}Cl^-]} \qquad (2)$$

where RCl is a variety of secondary and tertiary alkyl halides. It was found[41] that ionization in the 2-norbornyl and 2-methyl-2-norbornyl systems tended to be more exothermic than for other secondary and tertiary alkyl halides, but that the difference between their ΔH_i (-7.4 kcal/mol) was smaller than for other secondary-tertiary pairs. This result was verified by measurement of the heat of isomerization of 4-methyl-2-norbornyl cation to 2-methyl-2-norbornyl cation, found to be -6.5 kcal/mol.[42] This value, which is independent of initial state effects, is in excellent agreement with the gas phase results. The calorimetry experiments also indicate that ionization data for 2-norbornyl cation, unlike most other carbonium ions, were sensitive to the nature of the solvent. It was suggested that this arises from differences in the manner in which 2-norbornyl cation disperses charge (internal delocalization and external interaction with solvent molecules) as compared to other secondary cations. The gas phase results indicate that much, if not all, of these differences are attributable to unusual mechanisms for internal stabilization of charge.

Structural Considerations. Pyrolysis of bicyclo[2.2.1]heptan-2-methyl nitrite to yield 2-norbornyl radicals must be performed under conditions where the 2-norbornyl radicals themselves are thermally labile. This is illustrated in Figure 4, where the photoelectron band shape is found to change with temperature. The feature at ~ 7 eV, which decreases at lower temperatures, is thought to be a product of the thermolysis of 2-norbornyl radical. It may still be present in the spectra recorded at 385° C. Since still lower temperatures are not practical for thermal generation of free radicals, the extent to which the radical band is attributable to 2-norbornyl radical alone is unknown at present. However, the sharp feature at lower ionization energy does arise from 2-norbornyl radical, as evidenced by the observed isotope effect on the energy of the band.[31] Although only this part of the spectrum can be considered, its unique shape allows some conclusions to be drawn regarding the structure of 2-norbornyl cation in the gas phase.

Coincidence of vertical and adiabatic ionization potentials is evidence that little or no geometry change occurs on formation of the ion.[17,42] The presence of a Franck-Condon envelope extending to higher ionization energies indicates that, although changes in nuclear coordinates are minor, changes in force constants are important. It may be concluded, therefore, that in the gas phase the lowest energy structure of 2-norbornyl cation does not differ significantly from that of the radical. This does not rule out the possibility of the existence of degenerate structures which are reached by some rearrangement process, for example a Wagner-Meerwein rearrangement, since ionization directly to these structures from a static radical would have very low Franck-Condon factors. In fact, the part of the photoelectron band that may be obscured by ionization of product radicals may also contain a rather weak and broad contribution from these degenerate structures. These experiments do show, however, that 2-norbornyl cation is not likely to have a single, lowest energy, symmetrically bridged structure (**2**) in the gas phase.

This result is in contrast to conclusions drawn from experiments in condensed media.[9,10] It appears that interaction of 2-norbornyl cation with solvent molecules and possibly its counterion in the superacid medium may be substantial. Investigation of the importance of these interactions will be necessary to understand the origin of the apparent discrepancy between 2-norbornyl cation structures deduced from results in condensed and gas phases.

It is interesting to compare the spectrum of 2-norbornyl radical to those of cyclopentyl and cyclohexyl radicals, Figures 4, 7-9. Both cyclopentyl and cyclohexyl radicals have broad, featureless first photoelectron bands. This lack of structure may be due to resolution inadequate to resolve very low frequency ($\lesssim 350\ \mathrm{cm}^{-1}$) vibrations which may be excited on ionization. On the other hand, the lack of structure may be due to overlapping bands arising from ionization of nondegenerate conformations of the radicals, which have been identified by ESR experiments.[4, 43] Each transition would be between pairs of similar structures. Such overlapping would tend to smooth out any features present on bands arising from single conformations. Moreover, cyclohexyl cation rearranges essentially instantaneously to methyl cyclopentyl cation both in the gas phase and in solution,[41] so the Franck-Condon region for the cyclohexyl system may also include parts of the isomerization coordinate. 2-Norbornyl radical, on the other hand, is rigid and non-equilibrating,[8] and ionization to the structure most resembling it is the most probable process. The extent to which other low-lying or degenerate structures are probed is unknown. In view of the large nuclear motions involved, however, contributions from such structures are likely to be relatively small, as is also expected for cyclopentyl and cyclohexyl radicals.

A point of caution concerning the arguments presented here should be made. There is a possibility that the lowest energy structure for 2-norbornyl cation differs significantly from the radical structure. Transitions to this structure would be exceedingly weak, and not observable using the instrumental sensitivity available. An estimate for where the adiabatic IP to such a structure should be can be made by assuming the C_2-H bond dissociation energy in norbornane to be the same as that in cyclopentane, 92.5 kcal/mol. This would raise the heat of formation of 2-norbornyl radical to 28.0 kcal/mol, and, using the ionic heat of formation derived from the PA of norbornene, lower the IP to 6.67 eV. This is 0.17 eV or 3.8 kcal/mol lower than the energy taken to be the adiabatic IP in this work. In the most highly resolved spectra, this energy corresponds to a point ~ 0.08 eV lower than the onset of the main sharp peak. All efforts to determine whether the 2-norbornyl photoelectron band extended down this far indicated that it did not. Independent thermochemical data on 2-norbornyl radical are essential to resolve this point unambiguously. For the present, the band at 6.84 eV is assigned to be the adiabatic IP. Evidence for the reasonability of this assignment is found in the enhanced stability of 2-norbornyl radical as shown by ESR studies, leading to the expectation of a low homolytic bond dissociation energy in norbornane.

Conclusions

Generation of 2-norbornyl, cyclopentyl and cyclohexyl radicals by pyrolysis of the appropriate alkyl nitrites in a photoelectron spectrometer has allowed determination of their adiabatic and vertical ionization potentials. These data have been combined with free radical and proton affinity data from the literature to calculate thermochemical parameters for the three species. These data indicate that both 2-norbornyl radical and cation are unusually stable relative to other secondary species such as isopropyl, cyclopentyl and cyclohexyl. This stabilization is most pronounced in 2-norbornyl cation, being ~ 2/3 of that provided by methyl substitution at the trigonal site. It is also found that the lowest energy structure for 2-norbornyl cation in the gas phase is likely to be very close to that of the corresponding radical. These results indicate that the cyclopentyl and cyclohexyl systems are poor models for the 2-norbornyl system. Characterization of the mechanism by which 2-norbornyl cation achieves such extraordinary stability without significant nuclear rearrangement will allow understanding of the failure of the monocyclic cations as models for the bicyclic species.

Because of the thermal instability of 2-norbornyl radical, it is uncertain at present whether all of the photoelectron band arises from it. Consequently, no effort should be made to interpret the higher energy portion of spectrum in detail until all its features are fully understood. Generation of 2-norbornyl radical at room temperature by photolysis would be a good means of achieving this goal.

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CHAPTER V

The First Ionization Potential of 1-Propyl Radical by Photoelectron Spectroscopy

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Abstract

1-Propyl radical has been generated in a photoelectron spectrometer by pyrolysis of 1-butyl nitrite. The adiabatic and vertical ionization potentials (IPs) are 8.16 ± 0.02 and 8.37 ± 0.02 eV, respectively. Combination of the adiabatic IP and the heat of formation of the free radical gives a heat of formation of 210.8 ± 1.2 kcal/mol for the positive ion. There is evidence for a very weakly resolved vibrational progression on the low ionization energy side of the photoelectron band. Implications of the data for the existence of a local minimum in the $C_3H_7^+$ surface corresponding to a primary cation are discussed. Thermal decomposition of the radical into ethylene and methyl radical, but not propylene and hydrogen atom, was observed at higher temperatures.

Introduction

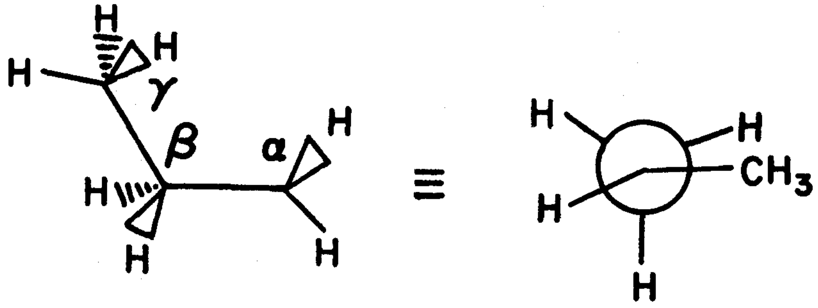
Although many ingenious experiments have been devised to trap or test directly for the presence of 1-propyl cation, this species remains elusive and poorly characterized. In both gas phase and solution, 1-propyl cation almost always isomerizes to a protonated cyclopropane or 2-propyl cation much more rapidly than it reacts.[1-3] This fact, together with the failure of theorists to find a well-defined minimum in the $C_3H_7^+$ surface corresponding to 1-propyl cation,[4, 5] has raised the question of whether or not this species exists with a finite lifetime. In order to determine accurately the energetics of formation of 1-propyl cation, photoelectron spectroscopy has been used to obtain the ionization potential of 1-propyl radical. In addition, it was hoped that the presence or absence of vibrational structure on the first photoelectron band would provide some information on features of the ionic potential energy surface in the vicinity of that structure of $C_3H_7^+$ most closely resembling 1-propyl radical. An advantage of the technique that makes it particularly suitable for the present study is that the electrons, not the ions, are detected, so that isomerization subsequent to ionization will in no way complicate the data.

The structure of 1-propyl radical is well-characterized by both theory and experiments.[6-13] It has been deduced from ESR data that the preferred conformation of the radical in solution has one of the $C{-}H_\alpha$ bonds eclipsing the $C_\beta{-}C_\gamma$ bond (see Figure 1). One study at 4K has suggested, however, that the $H_\alpha{-}C{-}H_\alpha$ plane actually oscillates between two minima located 30° on either side of the $C_\beta{-}C_\gamma$ bond.[10]

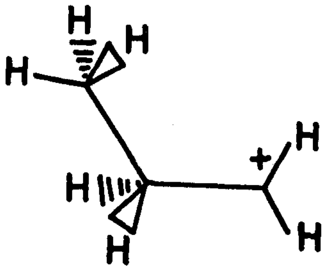
FIGURE 1

Structures of 1-propyl radical and cation

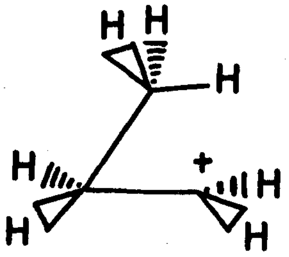
1-PROPYL RADICAL



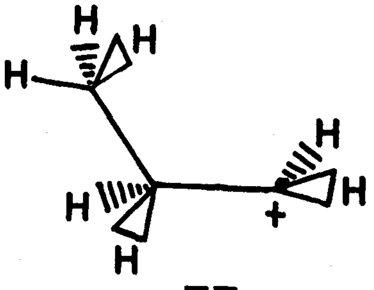
1-PROPYL CATION



I



III



II

Theoretical calculations indicate both possibilities to be very close in energy.[11, 12] The temperature dependence of the H_β coupling constants give a barrier for interchange of the two α hydrogens of ~ 400 cal/mol.[7] The barrier to internal rotation about the $C_\beta-C_\gamma$ bond is ~ 3.7 kcal/mol.[6] Infrared spectroscopy[13] has shown the stretching frequencies at the trigonal carbon in 1-propyl radical to be typical of centers having ~ sp^2 hybridization. From this it is possible to infer that the radical center is nearly planar; calculations[12] give on out-of-plane angle of ~ 11°. The measured out-of-plane bending frequency is very close to that in ethyl radical.[13]

The only information available on the structures of the $C_3H_7^+$ isomers comes from theory.[4, 5] Under the constraint of maintaining C_s symmetry, three local minima were found for the 1-propyl cation at the STO-3G basis set level.[4] As shown in Figure 1, these correspond to a conformation very similar to that of the radical (I) a conformation similar to the first except that the $C-H_\alpha$ bonds are staggered with respect to the $C_\beta-C_\gamma$ bond (II), and a structure resembling that of a distorted corner-protonated cyclopropane, having a C–C–C angle of ~ 83° (III). The three conformations are quite close in energy, with III being more stable than I by 2.5 kcal/mol at the 4-31G level. Improving the basis set to 6-31G* increases the relative stability of the distorted structure by 2.8 kcal/mol, leaving the more radical-like structures essentially unchanged.[5] It was concluded originally that the distorted structure corresponded to a minimum, while the others did not.[4] Subsequently, however, it was noted[5] that it was not clear whether or not the radical-like structures were local minima, presumably because no geometry optimizations have been performed using the higher-level basis sets, and C_s symmetry has been required.

Experimental Section

Photoelectron spectra were recorded on a spectrometer of standard design, which has been specifically modified to study products of gas-phase pyrolyses. It has been described in detail elsewhere.[14]

1-Propyl radicals were produced by thermal decomposition of 1-butyl nitrite, which was prepared from 1-butanol (Aldrich) using standard procedures.[15] Pyrolyses were performed over the range

$$CH_3CH_2CH_2CH_2ONO \rightarrow CH_3CH_2CH_2CH_2O + NO \qquad (1)$$

$$CH_3CH_2CH_2CH_2O \rightarrow CH_3CH_2CH_2 + CH_2O \qquad (2)$$

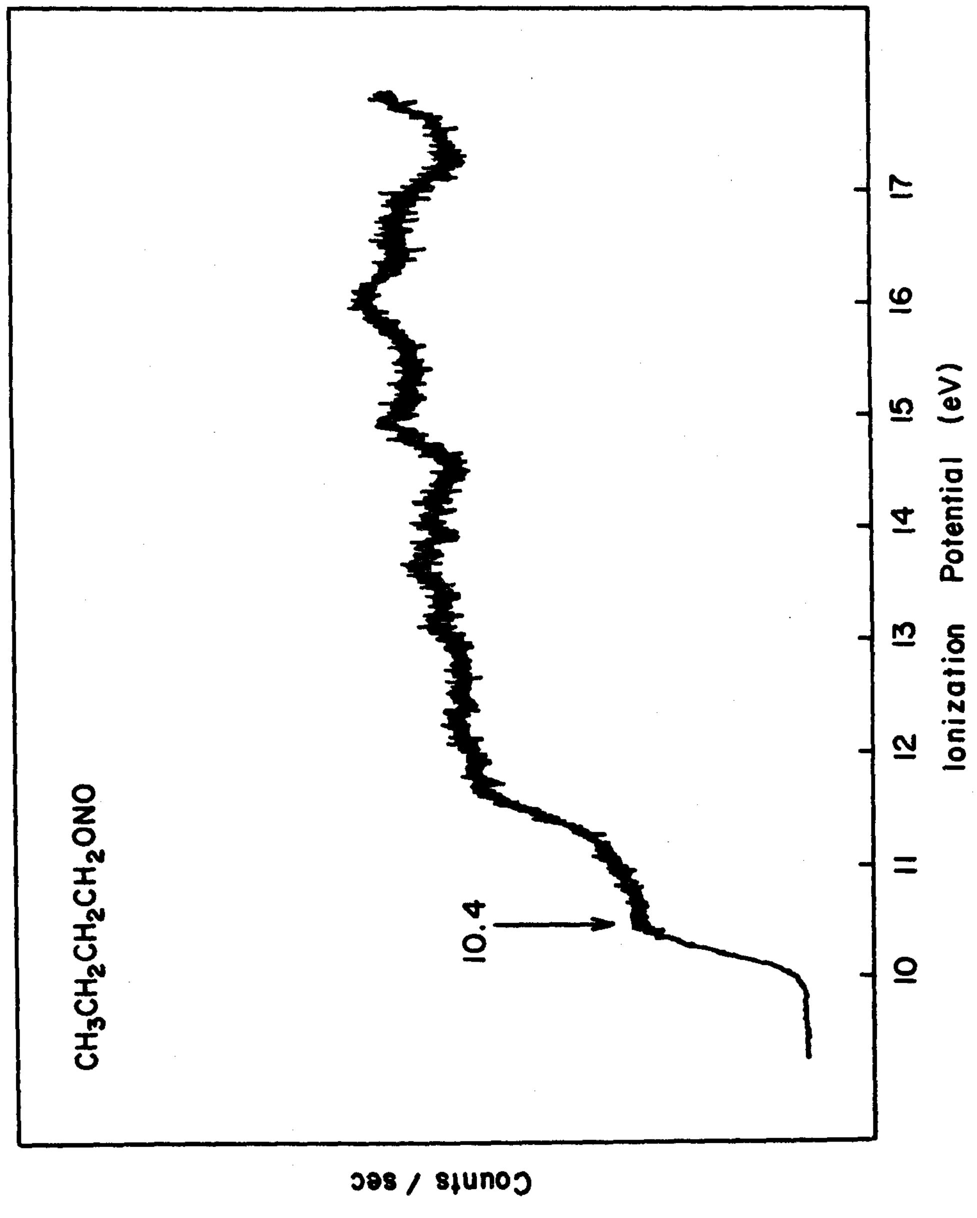
470-640° C. Spectra were recorded using HeI and NeI radiation. The energy scale was calibrated using the NO and CH_2O α and β bands, and argon when necessary. Resolution for these experiments was approximately 30 meV. Count rates for the radical band were $\sim 15\ s^{-1}$. The IPs reported here are the average of several determinations, and a reasonable estimate of the error is ± 0.02 eV. The vibrational spacings are ± 0.005 eV, since energy differences are more highly reproducible.

Results

The photoelectron spectrum of 1-butyl nitrite is shown in Figure 2. The ionization potential is determined to be 10.43 V.

FIGURE 2

HeI photoelectron spectrum of 1-butyl nitrite


$CH_3CH_2CH_2CH_2ONO$
10.4
10
11
12
13
14
15
16
17
Ionization Potential (eV)
Counts / sec

A NeI spectrum of 1-propyl radical is shown in Figure 3.[16] The vertical and adiabatic ionization potentials are determined to be 8.37 ± 0.02 and 8.16 ± 0.02 eV, respectively. The adiabatic IP is in good agreement with previous electron impact IPs of 8.10 ± 0.05 eV[17] and 8.13 ± 0.05 eV,[18] and a photoionization mass spectrometry estimate of ≤ 8.1 eV.[19] Combining the adiabatic IP with a heat of formation for 1-propyl radical of 22.6 ± 1 kcal/mol,[20] a heat of formation for 1-propyl cation of 210.8 ± 1.2 kcal/mol is obtained.[21]

A weakly resolved vibrational progression is just barely evident on the low ionization potential side of the band. The observed features, which appear in all spectra, comprise three members spaced by 0.063 eV, or 500 cm^{-1}.

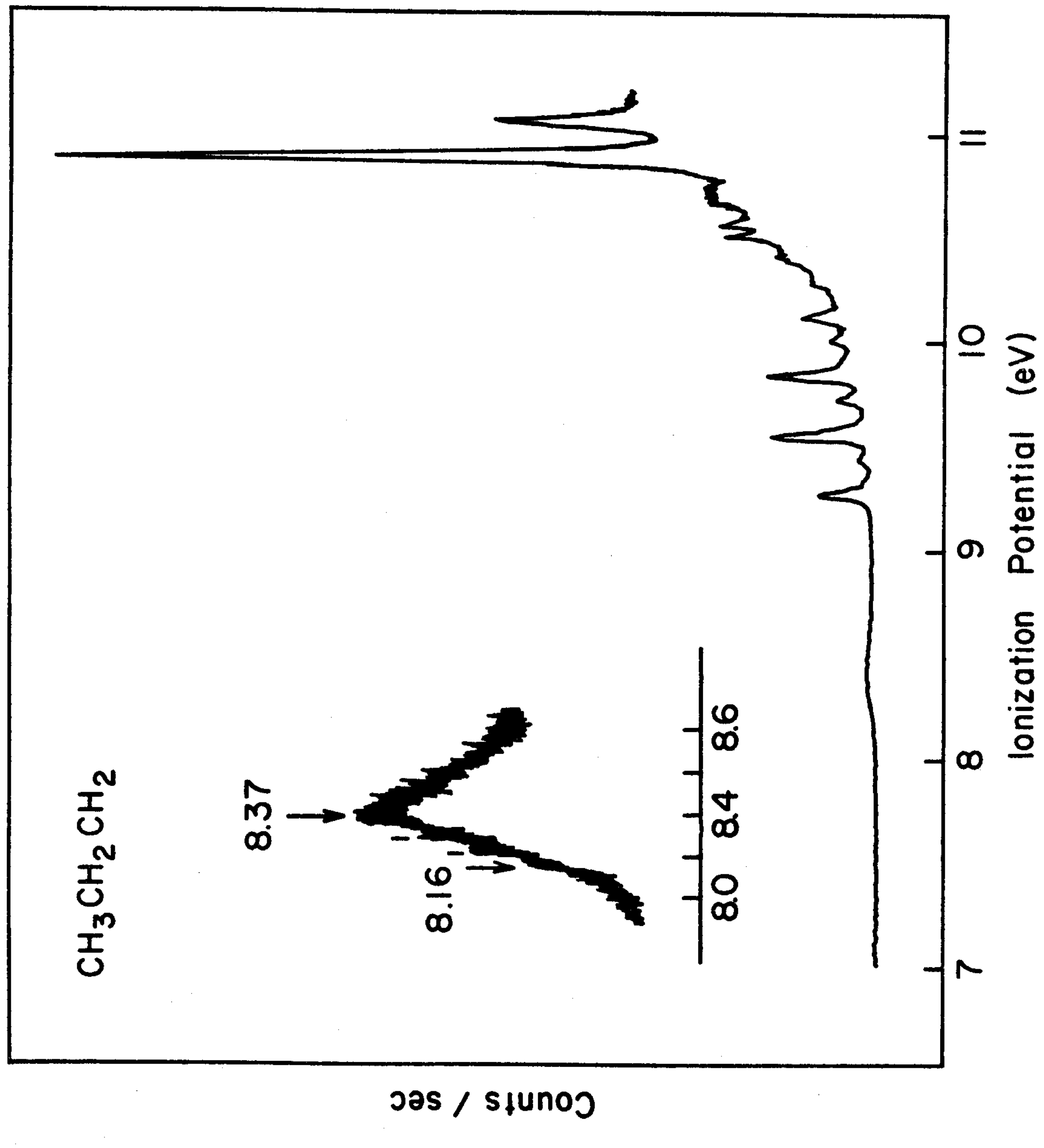
Above 500°, significant amounts of the 1-propyl radicals formed were observed to decompose via a reaction which has been observed

$$CH_3CH_2CH_2 \rightarrow CH_3 + CH_2CH_2 \qquad (3)$$

previously.[23] Evidence for this process is found in Figure 3. Ethylene is found at 10.51 eV,[24] and CH_3 is accidentally coincident with a member of the NO progression at 9.84 eV,[25] constituting ~ 30% of the band intensity. At low temperatures (~ 470°) a little propylene is formed. As the temperature is increased, however, none is found in the spectrum. This indicates that surface reactions may be responsible for the small amount present,[26] since homogeneous loss of H would be expected to become more important at higher temperatures. The relative rate of (3) is very much faster than homogeneous C_3H_6 formation, as is expected from the Arrhenius parameters of the two reactions.[27]

FIGURE 3

NeI spectrum of 1-propyl radical and other pyrolysis products of 1-butyl nitrite. The bands at 9.2-10 eV and 10.9 eV arise from NO and CH_2O, respectively.


CH$_3$CH$_2$CH$_2$
8.37
8.16
8.0
8.4
8.6
7
8
9
10
11
Ionization Potential (eV)
Counts / sec

Discussion

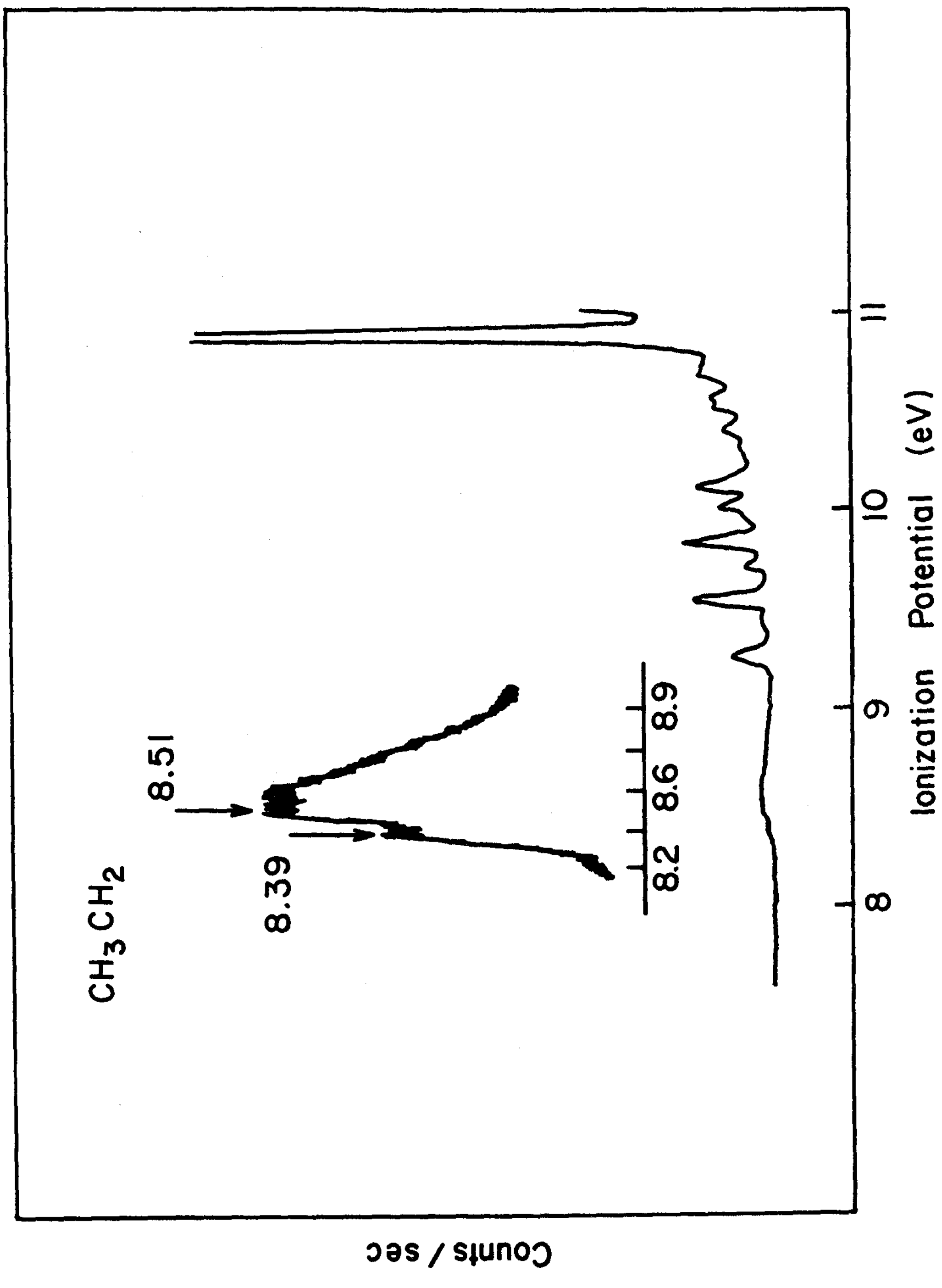
The band shapes obtained in these experiments can be used to examine some of the questions raised in the introduction regarding the structure and ease of rearrangement of the 1-propyl cation. In addition, the relative stabilities of the 1-propyl and 2-propyl cations in the gas phase and in solution can be compared.

The first photoelectron band of 1-propyl radical is broad, with a 0.3 eV difference between the adiabatic and vertical IPs. This is indicative of significant geometry change on ionization, which has also been found for other saturated alkyl radicals.[28] It is particularly interesting to compare the spectrum of 1-propyl radical with that of ethyl radical (Figure 4) taken from Ref. 28. The latter species has a single, well-resolved shoulder on the low-ionization energy side of the band, while 1-propyl radical has a very weakly resolved, three-member progression. Before the two systems can be compared further, however, some discussion of the origin of the 500 cm^{-1} progression should be made.

Both tert-butyl and isopropyl radicals undergo strong excitation of out-of-plane bending and symmetric skeletal stretching vibrations on ionization.[28] The corresponding frequencies for these modes in 1-propyl cation would be approximately 1000 cm^{-1} and 1100 cm^{-1}, respectively. Although it can be reasonably expected that these modes are in fact excited, they are too high in energy to correspond to the 500 cm^{-1} mode observed in the present experiments, and hence are probably not resolved. Comparison of the experimental structure for

FIGURE 4

NeI spectrum of ethyl radical, taken from Ref. 28.


CH$_3$CH$_2$
8.51
8.39
8.2
8.6
8.9
8
9
10
11
Ionization Potential (eV)
Counts / sec

1-propyl radical to the lowest energy theoretical one for the ion reveals that the major difference between them is the relative conformation of the terminal CH_2 group, which is $\sim 30^\circ$ out of the plane of the carbon chain in the radical, and perpendicular to the plane in the ion. Thus, assuming the ion to have C_s symmetry, excitation of torsions about the $C_\alpha - C_\beta$ bond would be expected, but would probably involve a frequency much lower than 500 cm^{-1}. If, however, C_s symmetry is not required, it is not clear to what extent the CH_2 conformations would differ between radical and ion. 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 coordinates would then be observed.[29] Returning to the ethyl radical spectrum shown in Figure 4, it can be seen that the band has a much more sharply rising low ionization energy side, and more high resolved structure than has been found for the 1-propyl radical spectrum (Figure 3). The open, or radical-like structure for ethyl cation is calculated to be unstable to a 1, 2 H^- shift to form a bridged cation.[28] This is just the motion required to form 2-propyl cation from its primary isomer. If both the ethyl and 1-propyl cations did not differ in any other respect, it would be expected that they would have very similar first photoelectron bands. The fact that the bands differ noticeably indicates that the 1-propyl cation potential energy surface differs from that of ethyl cation in the Franck-Condon region. This is not surprising, as 1-propyl cation has two isomerization channels, compared to only one for ethyl cation. Moreover, the energy difference between the open and bridged ethyl cations (~ 3 kcal/mol)[28] is much smaller than that for 1-propyl cation (~ 23 kcal/mol to form 2-propyl cation[28]). The isomerization coordinates are likely to be much more steeply descending in the latter case.

Although the 500 cm^{-1} progression of 1-propyl cation cannot be assigned, the fact that any vibrational structure was resolved at all is significant. It has recently been shown[30, 31] that light absorption to a saddlepoint in the upper state will normally give rise to vibrational structure in the spectrum (corresponding to modes not connected to the reaction coordinate) as long as the excited molecule dwells long enough in the saddlepoint region. If the molecule is excited to a steeply descending part of the reaction coordinate, any vibrational structure present will be too broadened to be resolved due to the short lifetime of the molecule in that region. Thus, it is possible to infer that 1-propyl cation is formed on a rather flat saddlepoint, or in an energy minimum having a very low barrier separating it from the isomerization coordinates. It should be noted that in the absence of a barrier to isomerization, the adiabatic IP may represent a vague limit which should be used with caution to evaluate the energetics of 1-propyl cation. The vertical ionization energy would be more significant in this case, since it represents the energetics of an ion with the same structure as the 1-propyl radical.

This inference is consistent with the failure to observe unrearranged 1-propyl cation experimentally.[1-3, 32] Although appearance potential measurements indicate that it is possible to form 1-propyl cation directly in the gas phase, this is a high energy process.[32] Attempts to trap and characterize these species have shown that they rearrange on a timescale of $< 10^{-10}$ sec.[1] In solution, it was reported[3] that ~15% of the propyl cations resulting from the deamination of labelled 1-aminopropane were unrearranged on reaction with OH^- to form propanol. However, based on similar studies with 1-aminobutane[33] and aminoisobutane,[34] it is likely that free primary cations are formed in only very small amounts. Rather, the diazonium ion from which the carbonium ion is derived undergoes S_N2 displacement by anions to yield the products directly.

The heats of formation of 1-propyl and 2-propyl cations are 210.8 kcal/mol and 187.3 kcal/mol,[28] respectively, corresponding to an energy difference of 23.5 kcal/mol between the two isomers. The third isomer, protonated cyclopropane, is probably intermediate between the two, but its heat of formation is not well-known.[32, 35] This difference of 23.5 kcal/mol can be compared to a recent estimate of 16.4 kcal/mol derived from lineshape analysis of proton exchange in 2-propyl cation by NMR.[36, 37] The experiments were performed in SO_2ClF-SbF_5 solution, over a 0-40° temperature range. The mechanism for the exchange was assumed to involve isomerization of 2-propyl to 1-propyl cation, followed by closure to protonated cyclopropane (which is necessary to account for ^{13}C scrambling). Regardless of the subsequent pathway, formation of 1-propyl cation is likely to be the most endothermic step, so 16.4 kcal/mol can be taken to be a measure of the difference in energy of the two isomers in solution. If this mechanism is correct, then solvent participation in the isomerization must be important. This can be understood as follows. It has been found[38] that small ions are much better solvated than large ones. 2-Propyl and 1-propyl cations, which are the same size, differ mainly in their charge distributions. The charge in 1-propyl cation is more localized, and so it is likely to be more stabilized by solvent interactions than 2-propyl cation, and its relative stability is increased by ~ 7 kcal/mol. If, however, the primary cation is not an intermediate, then the activation energy may reflect the energy difference between 2-propyl cation and protonated cyclopropane.

Chemical studies in both gas phase and solution, together with results from the present experiments, indicate that 1-propyl cation is a high-energy species whose primary role is as an intermediate structure in scrambling and isomerization processes. It remains to be determined, however, whether or not this structure corresponds to a local minimum. The failure of theoretical calculations to obtain the correct energy difference between 1-propyl and 2-propyl cations at the 6-31G* level[5] (~ 18 kcal/mol vs. the present value of 23.5 kcal/mol) indicates that the STO-3G structures used in the calculations may not be optimum. Because the direct formation of 1-propyl cation is a higher-energy reaction channel, it is usually generated with enough internal energy to isomerize very rapidly. It appears that experiments where the cation is formed at threshold are necessary to determine whether any barrier to rearrangement is present.

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CHAPTER VI

Thermal Decomposition Pathways of Alkyl Radicals by Photoelectron Spectroscopy. Application to Cyclopentyl and Cyclohexyl Radicals

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Introduction

Thermolysis systems involving organic free radicals as reaction intermediates are among the most difficult to characterize using more traditional chemical methods. Two of the most widely used of these are scavenging of radicals by various trapping agents present in the system, and direct sampling of a flowing system by mass spectrometry. Both of these methods have particular characteristics that may make the results obtained difficult to interpret. In general, free radicals can undergo many different types of reactions at rates comparable to scavenging rates. To completely characterize such a system, it is necessary that studies be done at many temperatures with varying amounts of scavenger present. In practice this is rarely done. When large (> six-seven carbons) radicals are being investigated, the numerous isomerization and fragmentation processes and their resulting products present an enormously complex system, even after the most thorough experiments. Extraction of a detailed reaction mechanism in such cases is often impossible. Mass spectrometric analysis in situ, on the other hand, allows direct observation of reactive intermediates formed in initial decomposition steps. Examples of applications of mass spectrometry to reacting systems such as flames and plasmas have been recently reviewed.[1] Techniques for quantitative studies of flowing pyrolysis mixtures at very low pressures have been developed by Benson.[2] Bayes has used photoionization mass spectrometry to study oxidation processes in hydrocarbons at intermediate pressures.[3] In favorable cases it is possible to distinguish structural isomers (species having the same mass) by measuring the appearance potential of the molecule being detected. Even in this case, however, it is difficult to identify small amounts of a species in the presence of a more abundant isomer having a lower ionization potential (IP), or in the presence of another molecule which fragments to yield the species observed at energies below its IP. Modulated beam mass spectrometry can be used to overcome some of the difficulties incurred in identifying the neutral precursor.[4]

In the present work, we explore the application of photoelectron spectroscopy to the detection of free radicals directly sampled from a high-temperature environment. It has been found that in general primary, secondary and tertiary alkyl free radicals have characteristic ranges of ionization potentials. In addition, the first photoelectron bands of hydrocarbon radicals having similar structures (acyclic, monocyclic, rigid bicyclic and conjugated π-type radicals) have similar Franck-Condon envelopes. Thus, even if free radical products whose bands are present in the photoelectron are species not previously studied, it is possible to identify them from their ionization energies and band shapes, and from stable products found in the spectrum.

Photoelectron spectroscopy has only been used in a few cases to study the mechanisms of chemical reactions. Bock and coworkers,[5, 6] for example, have studied products arising from pyrolysis of alkyl sulfides and acid chlorides. Thermolysis occurred outside the spectrometer, so only species having lifetimes of seconds or longer could be observed. Frost <u>et al.</u>[7] employed similar methods to study CS produced by the thermolysis of a substituted 1, 3, 4-triazoline-2-thione. In the present work, however, pyrolysis occurs inside the spectrometer, less than a centimeter away from the photoionization region. This configuration allows observation of species having lifetimes of ~ 1 msec. Particular systems studied using this instrumental configuration include the fate of reaction exothermicity in the thermal decomposition of azo compounds[8] and the mechanism of decomposition of 2-norbornyl radical.[9] This chapter focusses on the decomposition pathways of cyclopentyl and cyclohexyl radicals. These two species have been particularly well investigated using scavenging[10, 11] and mass spectrometric methods.[12] As will be discussed below, comparison of results from the three types of experiments allows characterization of the sensitivity of photoelectron spectroscopy, and enables resolution of some minor contraversy over the relative importance of particular unimolecular decomposition pathways.

Experimental Section

The photoelectron spectrometer used in these experiments is of standard design, and has been specifically modified to study the products of gas-phase pyrolysis. A full description of the instrument has been presented elsewhere.[13]

Cyclopentyl and cyclohexyl radicals were produced by the thermal decomposition of the corresponding alkyl nitrites, according to the reactions

$$\mathrm{RCH_2ONO} \rightarrow \mathrm{RCH_2O} + \mathrm{NO} \qquad (1)$$

$$\mathrm{RCH_2O} \rightarrow \mathrm{R\cdot} + \mathrm{CH_2O} \qquad (2)$$

where R is cyclopentyl or cyclohexyl. Cyclohexyl methyl nitrite and cyclopentyl methyl nitrite were prepared from the corresponding alcohols (Aldrich) using literature methods.[14] The alkyl nitrites have an activation energy of ~ 37 kcal/mol toward decomposition to NO and alkoxy radicals.[15] This is comparable to the energy required to decompose many of the alkyl radical products themselves, and it is possible to exercise a great deal of control over the extent of radical decomposition present in the spectrum. It is not possible, however, to observe product radicals whose barriers to decomposition are very much lower than ~ 30 kcal/mol, since the pyrolysis region is invariably too hot to allow their survival.

Pyrolyses were performed over a temperature range of 410-640° C. Spectra were recorded using both HeI and NeI radiation in order to ascertain which of the spectral features arose from HeIβ ionization. CH_2O and NO bands resulting from the nitrite decomposition were used to calibrate the spectra. Resolution for these experiments was 30-35 mV as determined from the width of Ar peaks. The identities of reaction products present in the spectra were determined by comparison to literature spectra, or, if possible, spectra of authentic samples recorded in our laboratory.

Results

Nitrites. The photoelectron spectra of cyclopentyl methyl nitrite and cyclohexyl methyl nitrite have been reported elsewhere,[9] and are not reproduced here.

Cyclopentyl Radical. The first photoelectron band of cyclopentyl radical, recorded at low temperature using HeI radiation is shown in Figure 1a. As discussed in Ref. 9, the adiabatic and vertical IPs have been determined to be 7.21 ± 0.02 and 7.45 ± 0.02 eV, respectively. As the furnace temperature is raised, the thermolysis products of the radical become prominent in the spectrum, as shown in Figure 1b. Cyclopentene[16] is present at the lower temperatures, but stays relatively constant after an initial increase. Allyl radicals, which have been previously reported,[13] and ethylene[17] are readily identifiable at higher temperatures.

Cyclohexyl Radical. The first photoelectron band of cyclohexyl radical has also been discussed more fully elsewhere.[9] The adiabatic and vertical IPs have been determined to be 7.15 ± 0.04 and 7.40 ± 0.04 eV, respectively. Figure 2 shows a lower temperature spectrum recorded with NeI radiation, and Figure 3 shows a HeI spectrum recorded at higher temperature. Reaction products are cyclohexene,[18] allyl radicals,[13] propylene,[16] and butadiene.[17] The relative amounts of cyclohexene and ring-scission products found in the photoelectron spectrum as a function of temperature show the same behavior as in the case of cyclopentyl radical.

Discussion

Through studies of the unimolecular decompositions of small alkyl radicals, it has been possible to formulate some generalizations concerning reactions to be expected.[19] Direct scission of C–H and

FIGURE 1

HeI photoelectron spectrum of cyclopentyl radical. CH_2O and NO are at 10.884 and 9.26 eV, respectively. The small features superimposed on the cyclopentyl band are due to HeIβ ionization of NO. (a) 485°C; (b) 556°C.

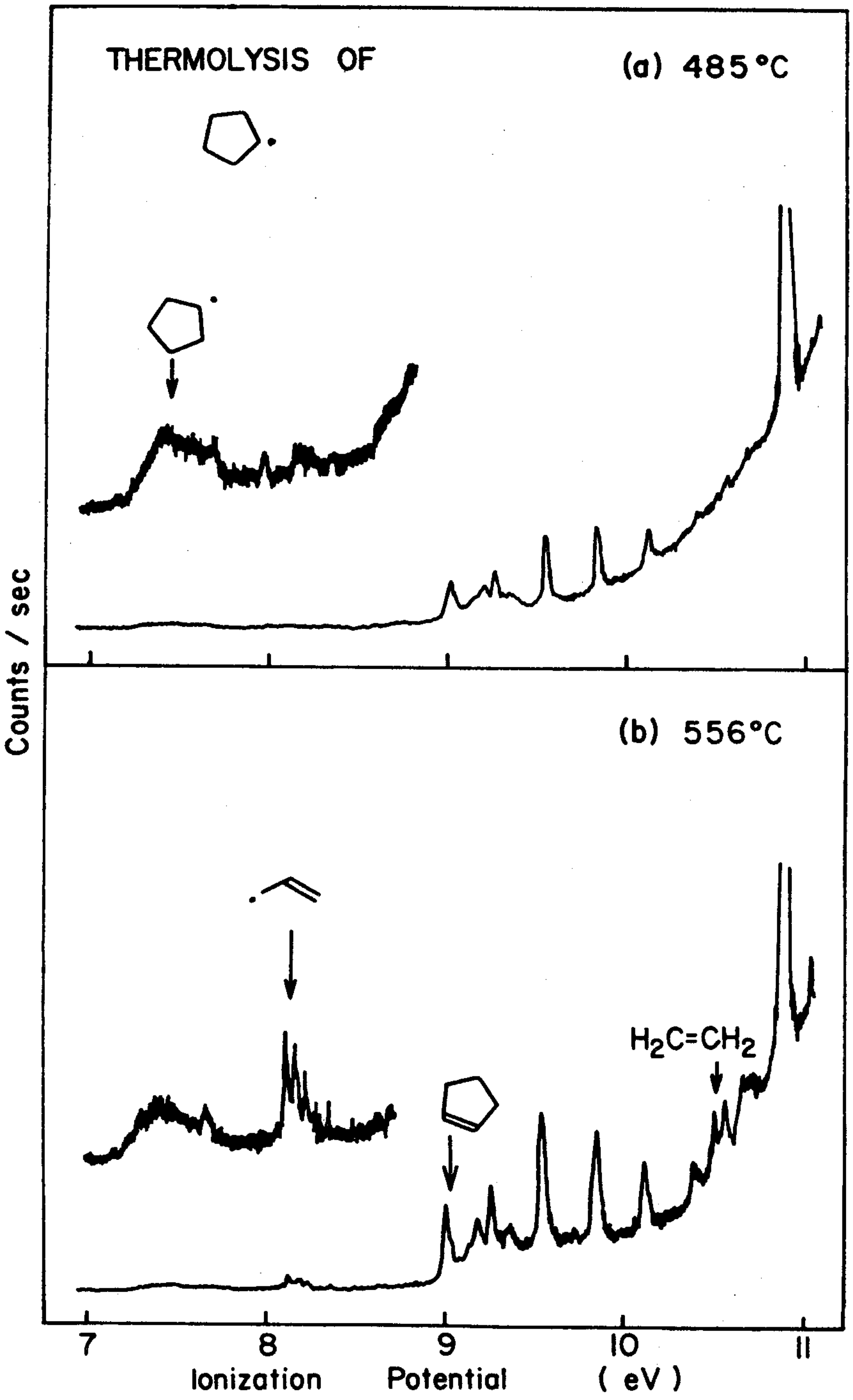

THERMOLYSIS OF
(a) 485°C
(b) 556°C
H$_2$C=CH$_2$
Counts / sec
7
8
9
10
11
Ionization Potential (eV)

FIGURE 2

NeI photoelectron spectrum of cyclohexyl radical at 474° C.

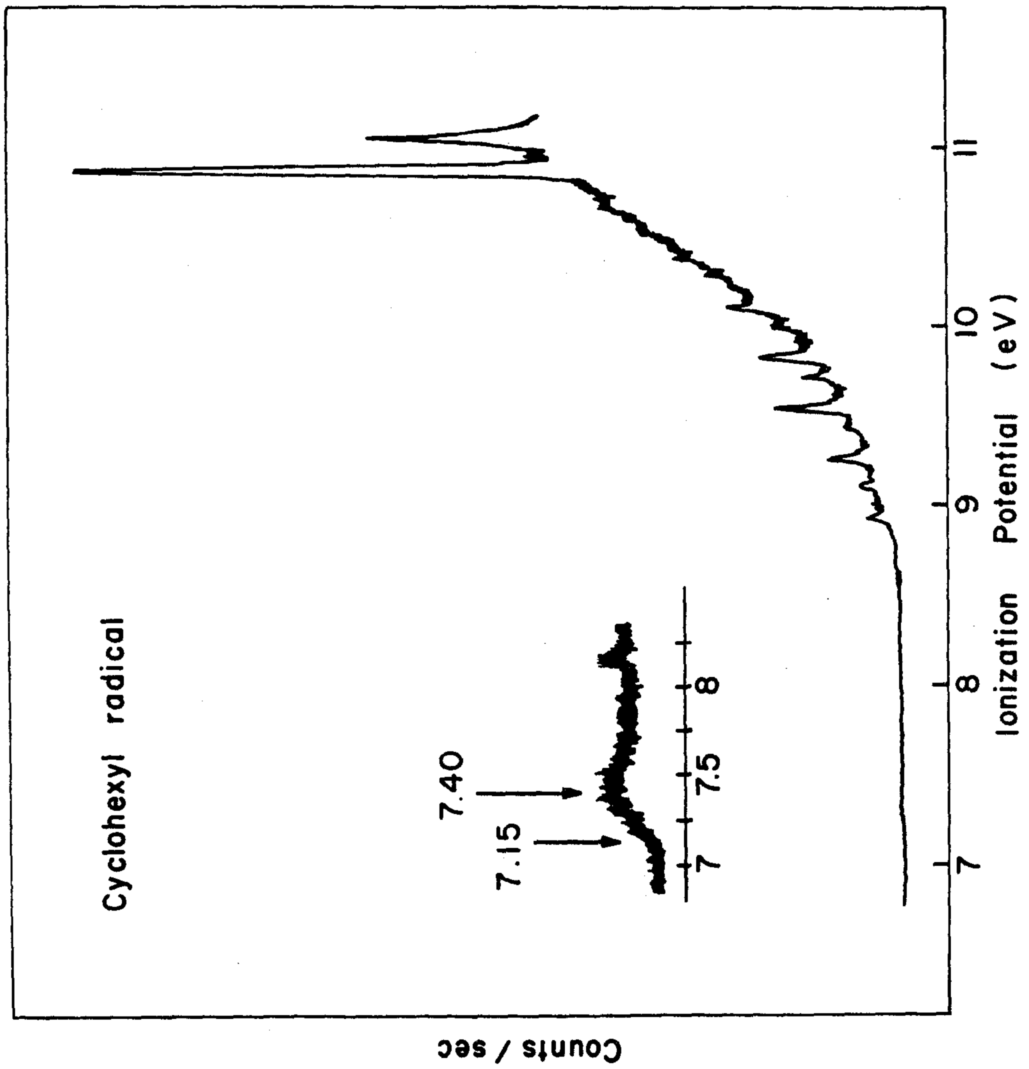
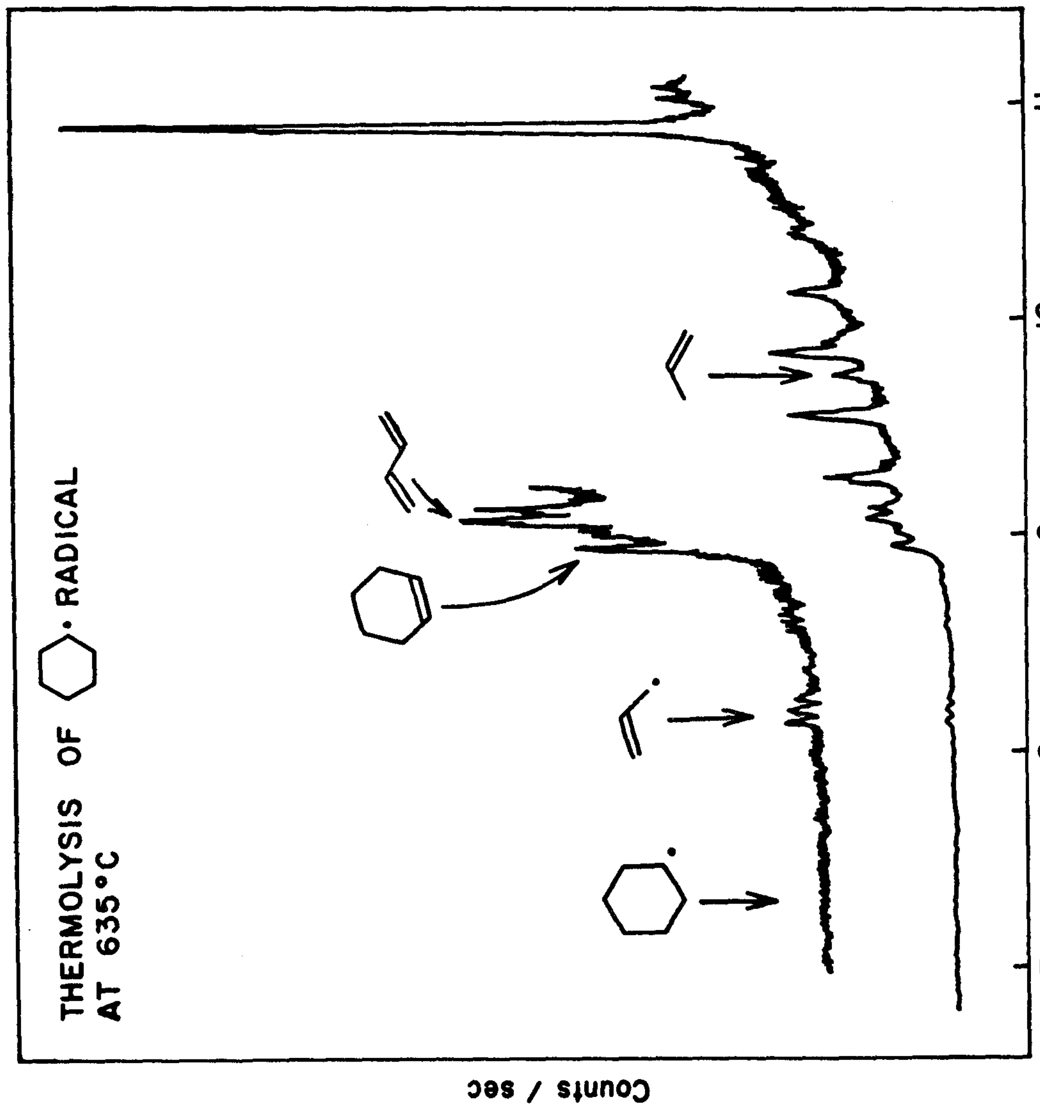

Cyclohexyl radical
7.40
7.15
7
7.5
8
7
8
9
10
11
Ionization Potential (eV)
Counts / sec

FIGURE 3

HeI spectrum of cyclohexyl radical at 635°C.


THERMOLYSIS OF · RADICAL
AT 635 °C
Counts / sec
Ionization Potential (eV)
7
8
9
10
11

C–C bonds β to the radical center is the most common process. In radicals where both fragmentation modes are possible, β C–C scission tends to predominate. Typical activation energies for β C–H scission are 35-40 kcal/mol, and A factors are in the area of 10^{13}. Activation energies for β C–C cleavage range from ~ 20-38 kcal/mol, depending on whether the radical in question is cyclic or acyclic. In general, primary acyclic radicals with long chains will have the lowest barriers to fragmentation. Isomerization of a free radical is a competitive process wherever 1, 4, 1, 5 and 1, 6 H shifts are possible. Arrhenius parameters for isomerization cannot usually be measured because the process is facile (i. e., not rate-determining) and occurs only in larger free radical systems whose chemistry is already complex.[20] A third process, direct elimination of H_2 to form an allylic radical, has been proposed.[21, 22] However, evidence for this reaction is indirect and, as will be discussed below, not substantiated by independent experiments.

In the remainder of this section, the photoelectron spectroscopic observations for cyclopentyl and cyclohexyl radicals will be discussed in light of mechanisms previously deduced using other experimental techniques. Results for other systems will be briefly described, and the utility of photoelectron spectroscopy for studies of chemical reactions will be evaluated.

Cyclopentyl Radical. Pyrolysis of cyclopentyl radical in the present experiments was found to produce cyclopentene, allyl radical and ethylene as the only major products (Figure 1). A decomposition scheme which can account for these is shown in Figure 4. The primary 1-penten-5-yl radical formed by opening of the cyclopentyl ring was not observed. Its ionization potential is not likely to differ much from that of other primary radicals (~ 8.1 eV), [23] and its first photoelectron band would lie underneath the allyl radical band. If significant amounts of 1-penten-5-yl radical had been present, a broad band would have appeared under the sharper allyl peaks. Thus it is unlikely that 1-penten-5-yl radical survives for as long as a millisecond in the heated region. Instead it appears to decompose rapidly to form allyl radical and ethylene.

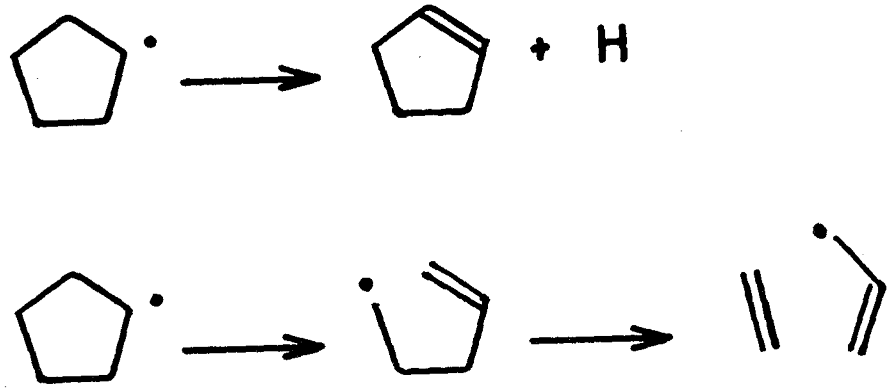
This scheme is in excellent agreement with results of a mass spectrometric investigation by Palmer and Lossing. [12] The configuration of their pyrolysis region was very similar to that used in the present work, and the same relative rates of cyclopentene and allyl radical production were observed. In addition to the major products, however, small amounts of propylene, biallyl, cyclopentane, and bicyclopentane were present. These species were not observed in the photoelectron spectrum, presumably because they were $\lesssim 1\%$ of the total reaction mixture (which is our limit of detectability). Lossing's observations and the present results indicate that disproportionation and recombination reactions, which probably give rise to the trace products, are unimportant under very low pressure conditions.

It is interesting to compare the photoelectron and mass spectrometric results to those obtained at higher pressures using scavenging techniques. [22, 24, 25] With an exception to be discussed

FIGURE 4

Mechanism for the thermal decomposition of cyclopentyl radical derived from the photoelectron results.

Thermal Decomposition of Cyclopentyl Radical



below, these experiments also corroborate the mechanism derived from the present work. Gunning and Stock[24] found that the lowest energy decomposition pathway for cyclopentyl radical was formation of ethylene and allyl radical. At higher temperatures, cyclopentene formation became important. Gordon[22] found cyclopentene at lower temperatures, with ethylene appearing as the temperature was raised. He ascribed the cyclopentene formed at lower temperatures to cyclopentyl-cyclopentyl disproportionation, and concluded that H atom loss from cyclopentyl radical became important at the same temperature as ring fission to form ethylene. This implies that both processes would have approximately the same Arrhenius parameters. The relative rates of ethylene and cyclopentene formation in the photoelectron and mass spectrometry experiments resemble those observed by Gordon. However, as noted above, disproportionation and recombination are unimportant under low-pressure, fast flow conditions. If the Arrhenius parameters for homogeneous decomposition of cyclopentyl radical into ethylene or cyclopentene are in fact comparable, then surface reactions of cyclopentyl radical at lower temperatures may be contributing to the overall decomposition in the photoelectron and mass spectrometry experiments.[12] Control experiments to assess importance of heterogeneous reactions have not been performed in the mass spectrometry,[12] scavenger[22, 24] or photoelectron experiments.

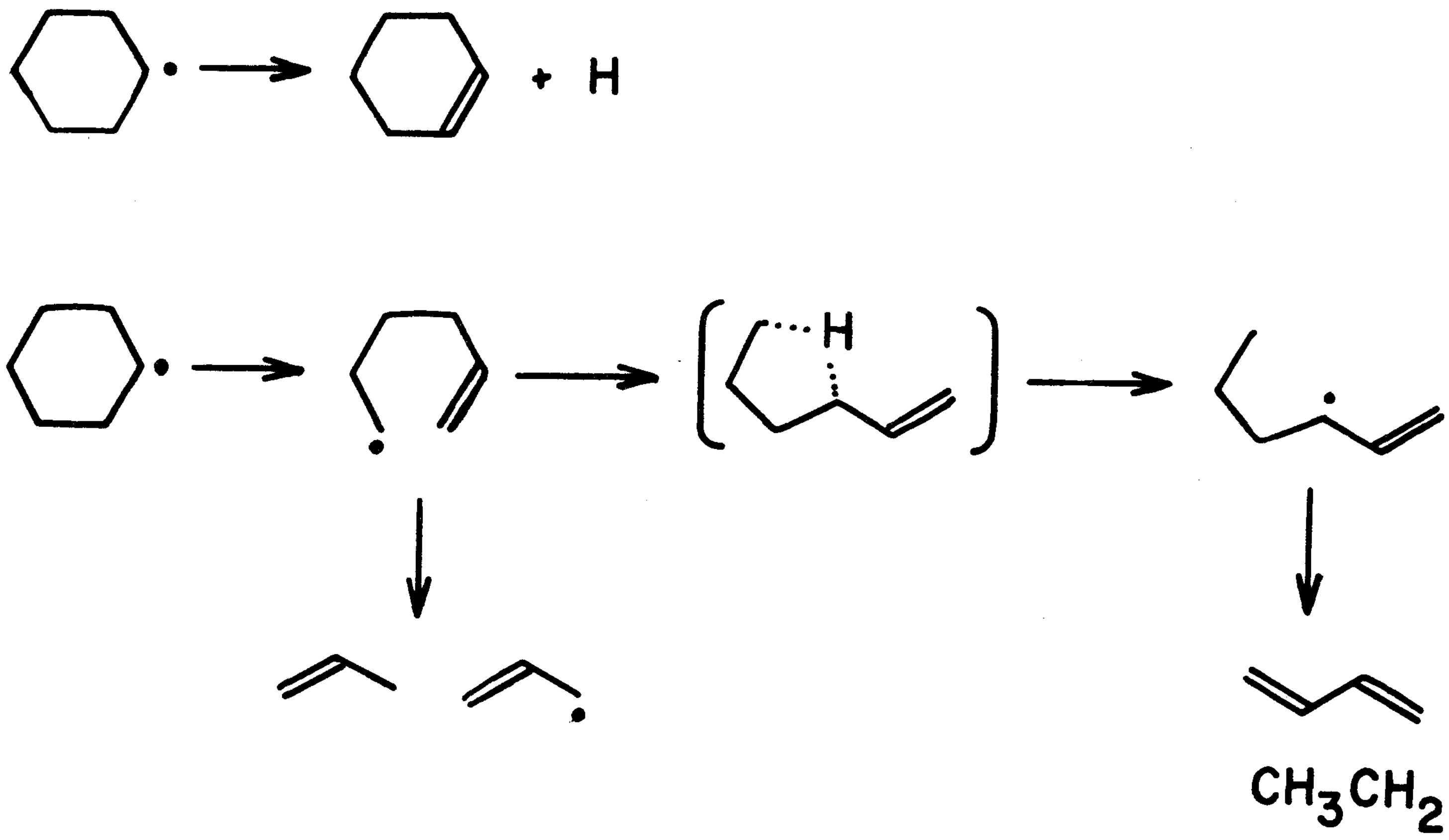
Gordon has proposed[10, 21, 22] that H_2 elimination from alkyl radicals to form allylic radical centers is extremely facile, with activation energies of ~ 35 kcal/mol.[22] For cyclopentyl radical, this proposal is based on evidence for cyclopentenyl radical formation during the reaction, and production of large quantities of H_2. It was not stated whether cyclopentadiene, a likely reaction product of cyclopentenyl radical, was observed. Neither cyclopentenyl radical, which has an IP of 7.00 eV,[26] nor cyclopentadiene[27] were observed in the present work, confirming earlier observations by Palmer and Lossing.[12] It would appear that the product distributions found by Gordon may be attributable to secondary reactions, rather than unimolecular decomposition of cyclopentyl radical. This conclusion is supported by chemical activation experiments,[25] which yield cyclopentyl radicals having ~ 40 kcal/mol of internal energy. 1-penten-5-yl radical was the only unimolecular product,[28] indicating that cyclopentyl radical does not form ethylene and allyl radical directly. Cyclopentenyl radical and cyclopentadiene were formed, but could be entirely accounted for by radical-radical reactions.

Cyclohexyl Radical. Although the initial decomposition steps of cyclohexyl radical are entirely analogous to those found for the cyclopentyl system (see Figure 5), the 1-hexen-6-yl radical formed is also capable of isomerizing. As shown in Figure 3, allyl radical, butadiene, cyclohexene, and propylene are all found in the photoelectron spectrum. The mechanism accounting for their formation is shown in Figure 5. This mechanism does not include a step shown to occur by chemical activation[25] and thermolysis[29] studies, but which was not observed in the present work. This is the isomerization of cyclohexyl radical to cyclopentyl methyl radical, which may or may not go

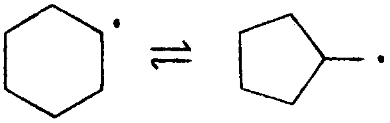
FIGURE 5

Mechanism for the thermal decomposition of cyclohexyl radical derived from the photoelectron results.

Thermal Decomposition of Cyclohexyl Radical



through an open-chain 1-hexen-6-yl radical.[22, 25] Evidence for this process is found in the large quantities of cyclopentyl methane



$\Delta H = 6.1$ kcal/mol (3)

recovered from the products.[25, 29] Studies of cyclization of 1-hexen-6-yl radical in solution[30, 31] have shown that both cyclic products are formed. Neither cyclopentyl methyl nor 1-hexene-6-yl radicals, nor any of their β C–H scission products were observed in the present experiments. The radical IPs would have been ~ 8.1 eV.[23] Apparently the barriers to β C–C cleavage for both C_6H_{11} isomers are too low to allow them to persist for the ~ 1 msec necessary to be observed in the photoelectron spectrum. The presence of butadiene in the spectrum is evidence for isomerization of 1-hexen-6-yl radical to the allylic 1-hexen-3-yl radical (via a 1, 4 hydrogen shift) with subsequent decomposition. The allylic radical has an IP estimated[32] to be 7.0 eV; it was not observed in the spectrum either.

The photoelectron data indicate that either cyclopentyl methyl or 1-hexen-6-yl radical fragments directly to form allyl radical and propylene. This is in disagreement with conclusions drawn from previous work,[29] where the reaction mechanism was constructed by assuming that isomerization of acyclic C_6H_{11} radicals would be very much faster than fragmentation.[10, 29, 34] The mechanism in that work[29] included rearrangements from an allylic radical to a simple secondary radical, with subsequent fragmentations to form simple primary or vinylic radicals. These are all likely to be very high energy pathways, and probably do not compete very well with direct fragmentation. In fact, the observed products[29] do not require such complex rearrangements, but are accounted for quite well by the mechanism in Figure 5. The present work provides evidence that such generalizations as are made by Gordon[10, 29, 34] concerning reactions of larger free radicals should be viewed with caution unless the proposed intermediate radicals have been directly detected.

As in the case of cyclopentyl radical, Gordon[10, 29] has proposed H_2 elimination to form cyclohexenyl radical to be important in the cyclohexyl system. No evidence for this process was found in the present experiments, where 1, 3 cyclopentadiene[16] and cyclohexenyl radical (~ 7. 0 eV)[32] would be expected to be found in the spectrum. This is in concordance with chemical activation results.[25]

As noted in the experimental section, cyclohexene was observed at lower temperatures than allyl radical and butadiene resulting from C–C scission in cyclohexyl radical. This is what was found for cyclopentyl radical, and the remarks concerning the importance of heterogeneous processes in that system are applicable for cyclohexyl radical also.

Results for Other Systems. The thermolysis of 2-norbornyl radical and 1-propyl radical has been investigated using photoelectron spectroscopy. The results for 1-propyl radical confirmed earlier work using mass spectrometry, and are described elsewhere.[35] 2-Norbornyl radical, whose chemistry had not been previously characterized by mass-spectrometry or scavenging, provided a particularly interesting subject for study. The results of the photoelectron experiments are discussed in a separate paper.[9]

Preliminary results[36] for cyclobutyl radical have been obtained. Since it was possible to observe this species under conditions similar to those required for cyclopentyl and cyclohexyl radicals, it is not likely that the activation energy for ring opening to form allyl carbinyl radical is very much different than that for β C–C cleavage in the C_5 and C_6 species. This observation, together with those of others,[20, 25,37] indicates that the E_a for ring-opening in cyclobutyl radical of 18 kcal/mol reported by Gordon[38] is seriously in error. Experiments in progress will serve to indentify the decomposition pathways of cyclobutyl radical.

Assessment of the Utility of Photoelectron Spectroscopy for the Study of Free Radical Reactions. Cyclopentyl and cyclohexyl radicals are good examples of the added insight that photoelectron spectroscopy can bring to free radical chemistry. Elimination of complications introduced by scavengers, disproportionation and recombination allows the mechanism of the initial reaction steps to become immediately identifiable. Restriction of observable reaction times to ~ 1 msec is also important. The results of the present work indicate that, at moderate temperatures, most of the initial chemistry takes place on that timescale. Thus it is likely that very few of the products observed in scavenging experiments result from free radicals formed in decomposition steps of interest.

Photoelectron spectroscopy will be a very powerful tool for qualitative analysis of reacting systems, particularly when combined with mass analysis of the ions formed. The results can be compared to those of scavenging experiments to characterize more fully the role of bimolecular reactions in free radical systems. In order to observe thermolysis of the less stable radicals, however, it will be necessary to produce the radical of interest by photolysis or atom-molecule reactions, so that the pyrolysis temperatures can be more easily controlled. This would allow study of processes having activation energies of $<$ 20 kcal/mol, which is impossible using pyrolysis of alkyl nitrites.

It is unlikely that photoelectron spectroscopy will be very useful in the determination of rate constants. Calibration of photoelectron band area vs concentration will have to be made for each individual radical, and some means of monitoring instrumental performance during the experiments devised. Moreover, bands of different species often overlap (as shown, for example, in Figure 3), and deconvolution of the composite bands is not likely to be a trivial process. Finally, the radicals generated in the present work have temperatures that are poorly defined, probably 200-300° lower than the stated furnace temperature. Establishment of thermal equilibrium is essential to obtain rate constants, but will bring with it the added complication of hot bands in the photoelectron spectrum. It appears at present that scavenging and emission and absorption of light are still the most useful methods for obtaining quantitative rate data.

As a final point, photoelectron spectroscopy is in no way limited to the study of pyrolysis systems. Any gas phase system involving reactive intermediates will be amenable to study, for example flames, discharges, photolysis mechanisms, and radical-radical reactions. It is conceivable that observation of electronic and, in suitable cases, vibrational excitation will be an important application using instruments designed to work with species having lifetimes of 10^{-9}-10^{-6} sec.

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$$IP = \Delta H_f(R^+) - \Delta H_f(R\cdot) = D(R^+H^-) - D(R-H) - \Delta H_f(H^-) + \Delta H_f(H\cdot).$$

The $\Delta H_f(H-)$ was taken to be 34.7 kcal/mol at 298 K.

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CHAPTER VII

Thermal Decomposition of Cyclic and Bicyclic Azo Compounds by Photoelectron Spectroscopy. Implications for the Fate of Energy Released on Fragmentation

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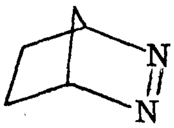
Abstract

The gas phase pyrolyses of 2, 3-diaza-bicyclo[2. 2. 1]heptane, 3, 4-diaza-exo-tricyclo[4. 2. 1. $0^{2,5}$]non-3-ene, and 3, 3, 4, 4-tetramethyldiazetine have been performed in the inlet system of a photoelectron spectrometer. By analysis of the observed internal energy content of the newly formed products, it has been possible to put limits on the amount of reaction exothermicity released to vibration of the nitrogen fragment, which appears to acquire very little of the available energy. The implications of this result are discussed in terms of a model which has been proposed for distinguishing concerted and stepwise unimolecular elimination reactions.

Introduction

An operational criterion for the concertedness of bond-breaking in gas-phase unimolecular elimination reactions has been proposed by S. H. Bauer.[1] This criterion states that, if bond-breaking were truly concerted, the separating fragments would be poorly coupled to one another, and any energy released after passing through the transition state would be trapped in the fragments rather than delocalized throughout the molecule. In particular, fragments whose structures as free molecules differ greatly from those in the parent species would trap energy in the form of geometrical distortion. Examples of such fragments are those which acquire a higher bond order as a result of reactant pyrolysis, such as N_2 from cyclic azo compounds, or alkenes formed in 1, 2 elimination reactions. In these two examples, it would be expected that reaction exothermicity would manifest itself primarily by the appearance of vibrational excitation in the nitrogen and organic moieties, respectively.

Azo compounds 1-3 have been prepared in recent years, and the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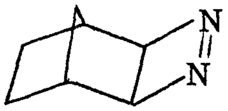
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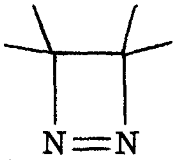

3

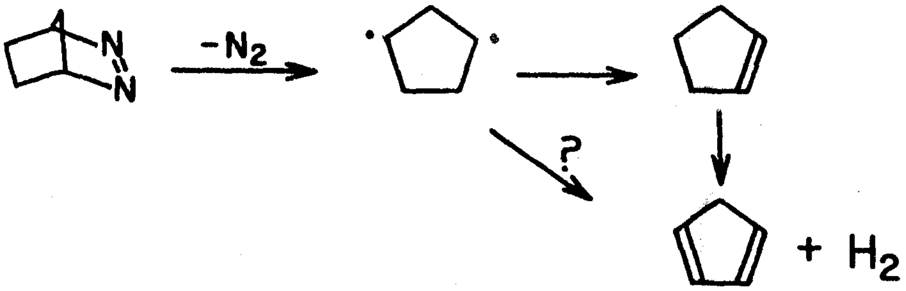
mechanisms of their thermal decomposition have been investigated.[2-8] A summary of the reaction pathways is shown in Figure 1. The energetics of the decompositions, to be discussed below, are presented in Figure 2. Using Bauer's criterion, simultaneous rupture of the

FIGURE 1

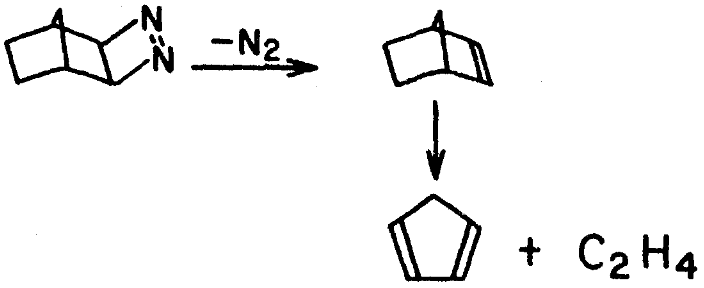
Thermal decomposition pathways for azo compounds 1-3.

Thermolysis Mechanisms

(a)



(b)



(c)

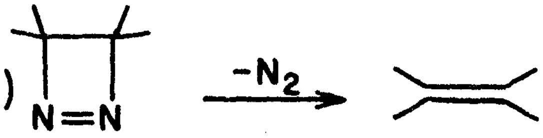
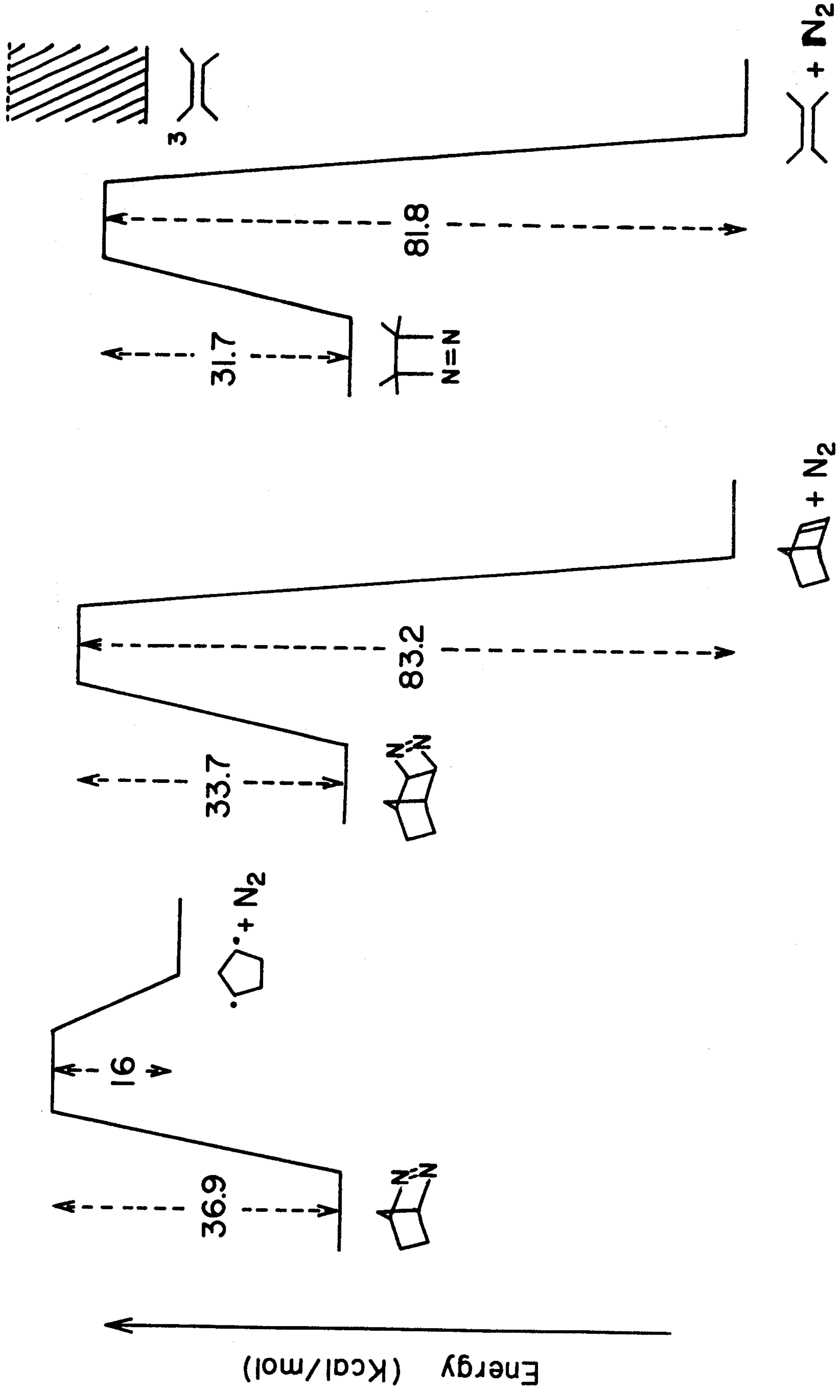


FIGURE 2

Diagram of reaction energetics of azo compounds 1-3.


Energy (Kcal/mol)
36.9
16
+ N2
33.7
83.2
+ N2
31.7
N=N
81.8
3
+ N2

C–N bonds would be expected to produce vibrationally excited N_2, and, in the case of 3, 2,3-dimethyl-2-butene, neither of which can usually be detected in kinetics experiments without the use of special spectroscopic techniques. A stepwise mechanism involving a diazenyl biradical would, on the other hand, be likely to promote extensive delocalization of reaction exothermicity throughout all degrees of freedom of the fragments, unless the biradical has a lifetime of one or two vibrational periods or less.

In order to attempt to distinguish between the possible mechanisms, a search has been made for vibrational excitation among thermolysis products of 1-3. The experimental technique used in this investigation is gas phase pyrolysis under low pressure, fast flow conditions in the inlet system of a photoelectron spectrometer (PES). Several aspects of this technique make it particularly suitable. In the apparatus used, pyrolysis occurs immediately outside the photoionization region, so that species with lifetimes of ~ 1 msec at pressures of 50-100 mTorr are readily observable. If the photoelectron bands of the products exhibit vibrational structure, well-defined hot bands appear in the spectrum when the products are excited. Although the photoelectron spectrum of a pyrolysis mixture is usually quite complex, consisting of bands arising from several species, if one or more of those species has bands with sharply resolved structure, its spectrum is easily identifiable. For example, N_2 is readily recognized in the presence of organic products. Moreover, vibrationally excited N_2 produced in a microwave discharge has been shown to be readily detected by photoelectron spectroscopy,[9] with the highest level of excitation (up to $v'' = 7$) being observed when the discharge was placed immediately outside the photoionization region. Thus, the use of photoelectron spectroscopy in azo decomposition experiments provides a simple, direct method of qualitatively analyzing for the presence of vibrational excitation in nascent products. It cannot, however, yield quantitative information on the extent of excitation without complete understanding of photoionization cross sections and analyzer sensitivity as a function of electron kinetic energy. Nevertheless, as will be discussed below, the qualitative results obtained in the present work serve to narrow the range of possible decomposition mechanisms for cyclic and bicyclic azo compounds.

Experimental Section

Instrumentation. The photoelectron spectrometer used in the present experiments is home-built and of standard design. It has been specifically modified to study the products of pyrolyses, and has been described in detail elsewhere.[10]

Materials. Compounds **1**-**3** were prepared using literature methods.[6, 11, 12]

Photoelectron Spectra. All spectra were recorded using HeI radiation. Some were obtained using a ratemeter and chart recorder, while more recent experiments involved a Tracor-Northern NS 570A multichannel scaler with 4K memory. Pyrolyses were performed over a range of temperatures (500°-800° C) under conditions of complete diazene decomposition. Heating of authentic samples of N_2 and 2, 3-dimethyl-2-butene produced no evidence of vibrational excitation, indicating that thermal equilibrium is not achieved during the short residence times inside the pyrolysis region. Norbornene was completely decomposed, and cyclopentene partially so under conditions necessary for complete thermolysis of the parent azo compounds.

Resolution was 30 meV for these experiments. The energy scale was calibrated using both the N_2 bands and Argon introduced as an internal standard. Based on previous experience with the spectrometer, a mimimum of approximately 5% of the N_2 would have to be excited to appear as signal above the noise in the spectrum. This limit is a little higher for species whose photoelectron bands are not as sharp. Thus, the conclusions presented here should be taken to be valid within a 5% error margin.

Results

The photoelectron spectra of 2, 3-diazabicyclo[2. 2. 1]hept-2-ene (**1**),[13] 3, 4-diaza-*exo*-tricyclo[4. 2. 1. $0^{2,5}$]non-3-ene (**2**),[14] and 3, 3, 4, 4-tetramethyldiazetine (**3**)[15] have all been reported previously. The spectra recorded in the course of the present work are in excellent agreement with them.

The pyrolysis spectra are shown in Figures 3-5. They are consistent with the mechanisms shown in Figure 1, as evidenced by the appearance of the appropriate products in the photoelectron spectra. The scheme is consistent with the results of previous kinetics experiments using more conventional techniques for **2** and **3**. In the earlier

FIGURE 3

Photoelectron spectrum of pyrolysis products of 2, 3-diazabicyclo [2. 2. 1]heptene. N_2, cyclopentene and cyclopentadiene can be identified.

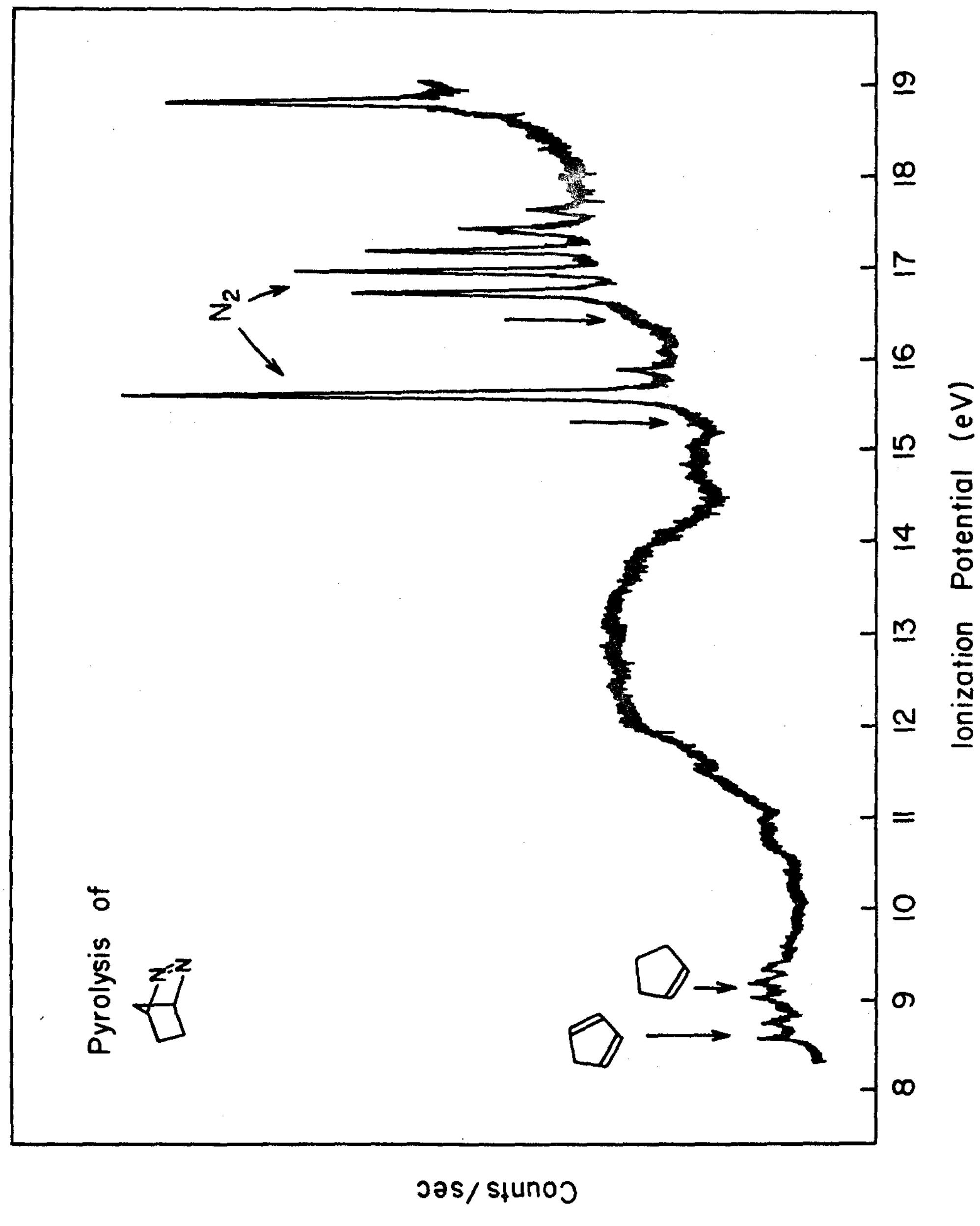

Pyrolysis of
N
N
N_2
Counts/sec
Ionization Potential (eV)
8
9
10
11
12
13
14
15
16
17
18
19

FIGURE 4

Photoelectron spectrum of pyrolysis products of 3, 4-diaza-exo-tricyclo-[4. 2. 1. $0^{2,5}$] non-3-ene. N_2, cyclopentadiene and ethylene are present.

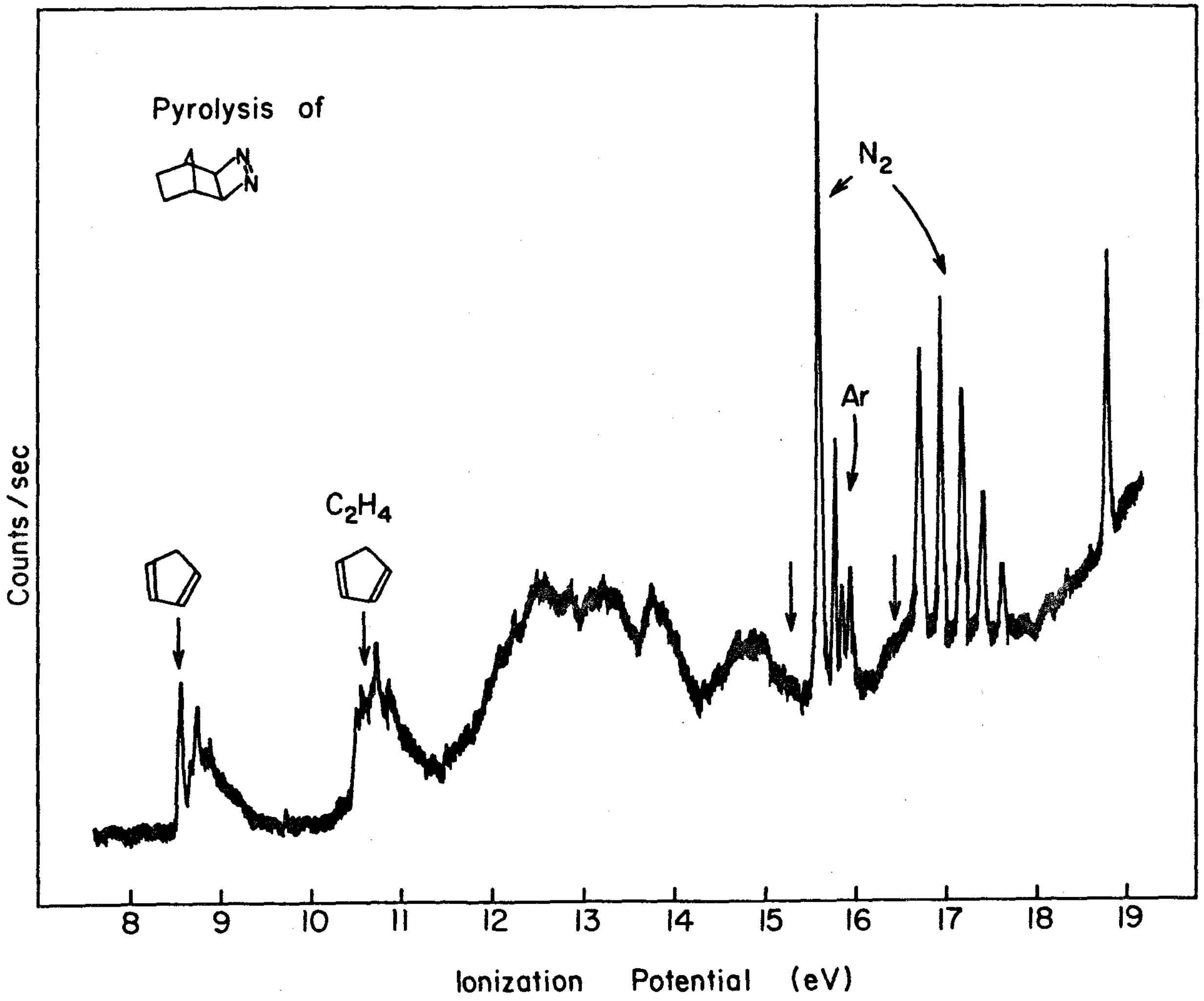
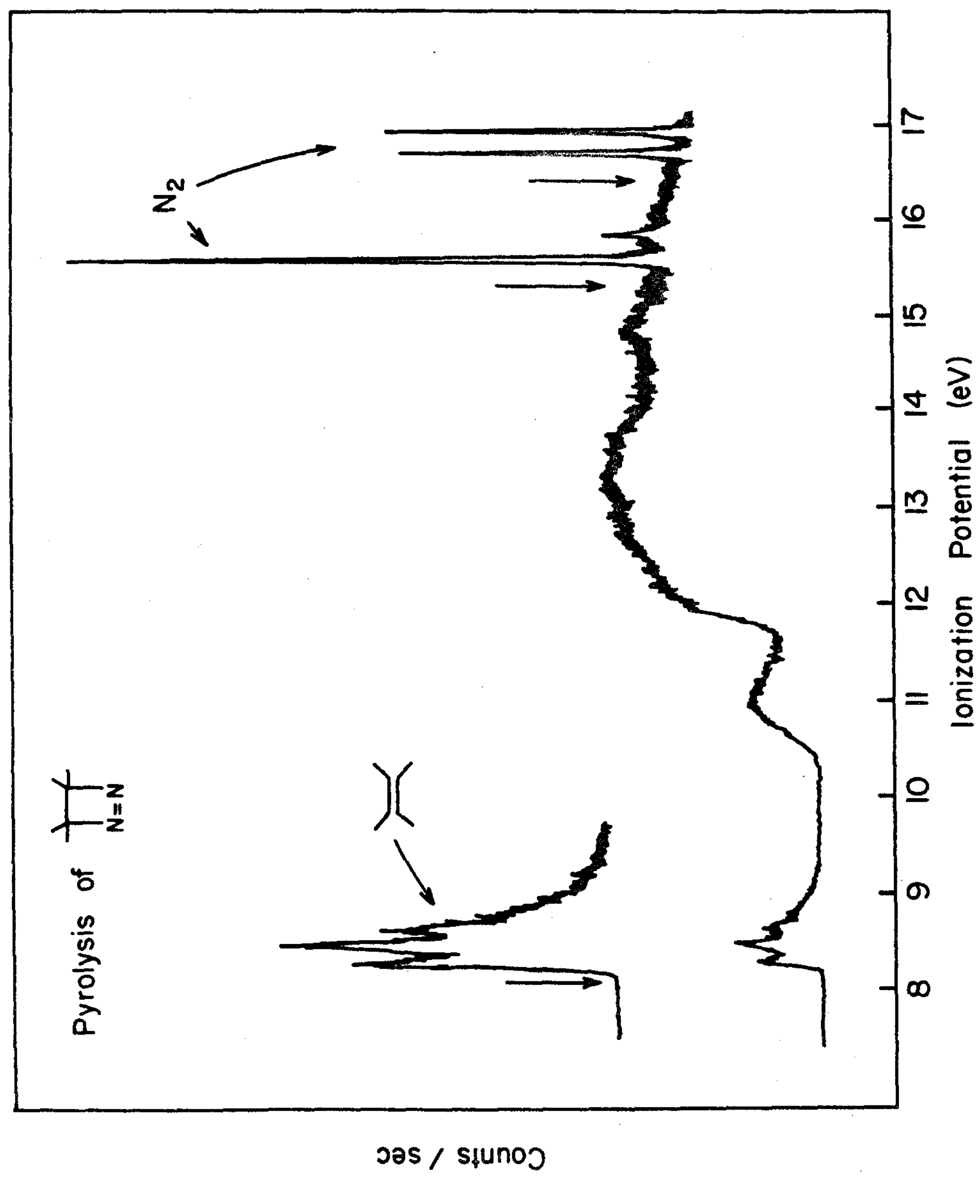

Pyrolysis of
N
N
N_2
Ar
C_2H_4
Counts / sec
8
9
10
11
12
13
14
15
16
17
18
19
Ionization Potential (eV)

FIGURE 5

Photoelectron spectrum of pyrolysis products of 3, 3, 4, 4-tetramethyldiazetine. N_2 and 2, 3-dimethyl-2-butene are present.


Pyrolysis of
N=N
N_2
8
9
10
11
12
13
14
15
16
17
Ionization Potential (eV)
Counts / sec

study,[6] diazetine 2 was pyrolyzed in the gas phase at somewhat higher pressures and lower temperatures, and thus the only organic product observed was norbornene. The higher temperatures required to obtain nearly complete diazetine decomposition in the present experiments were sufficient to completely decompose the norbornene to cyclopentadiene and ethylene.[16] The latter two are the only organic products observed.[17] Thermolysis of 3 in solution[8] yielded only N_2 and 2, 3-dimethyl-2-butene, exactly as observed here. The results obtained for 1 are not directly comparable to previous solution studies,[2-4] which gave N_2 and bicyclo[2. 1. 0]pentane as products. As shown in Figure 3, the recognizable products are cyclopentene[18] and cyclopentadiene.[17] Bicyclo[2. 1. 0]pentane, which has adiabatic and vertical ionization potentials of 8. 7 and 9. 5 eV,[18] respectively, may also be present, but cannot be distinguished underneath the more salient features of the cycloalkenes. It must be inferred that the chemically activated bicyclo[2. 1. 0]pentane formed from the 1, 3-cyclopentadiyl biradical is not appreciably stabilized at low pressures, and rearranges to form the more stable isomer, cyclopentene. This in turn partially decomposes to give cyclopentadiene and H_2.[19] The photoelectron band of H_2 underlies those of N_2, and is not very prominent in the spectrum.

As expected, no photoelectron bands identifiable as belonging to a biradical were observed. The expected lifetimes of such species are much shorter than the 1-5 msec residence time in the heated furnace, and they are likely to have decomposed or rearranged long before reaching the photoionization region.

No effort has been made to assess the importance of surface reactions. Collisions with the walls predominate at these pressures, and it is conceivable that all the observed decomposition could be taking place there. There is independent evidence, however, that this may not be a serious problem. The quartz tube where decomposition occurs is actually coated with a thin carbonaceous layer, which acts as a surface conditioner, and is not likely of itself to promote surface-catalyzed reactions. This latter point is supported by work characterizing the performance of the very low pressure pyrolysis (VLPP) apparatus of Benson,[20] which is very similar to the assembly used in the present work. Also, in experiments investigating the thermal decomposition of n-propyl and cycloalkyl radicals,[21] minor processes attributable to surface reactions were found to occur only at temperatures much lower than those used for pyrolysis of the azo compounds. Presumably, this is because desorption rates increase with temperature, and homogeneous reactions become more important.

Hot bands associated with vibrationally excited 2, 3-dimethyl-2-butene and N_2, if present, can be readily identified. In the case of the olefin, a peak or peaks should appear at 0. 207 eV (1674 cm^{-1})[22] lower energy than the adiabatic ionization potential; where the spacing corresponds to a quantum of $-C=C-$ stretching energy in the neutral butene. Vibrationally excited N_2 has been observed previously[9] as noted above. Peaks displaced to lower energy by an amount equal to the stretching frequency in neutral N_2 can be easily distinguished. Examination of Figures 3-5 reveals that no hot bands are found in the spectra. (Their expected locations are marked by arrows.) This implies that pyrolysis of the parent azo compounds 1-3 does not generate products with enough internal energy for the excitation to be observed by PES. This result can be analyzed to provide limits on the fraction of reaction exothermicity channelled into internal degrees of freedom in the products.

Discussion

As shown in Figure 2, the energy available at the transition state in diazetines 2 and 3 is considerable. Thermochemical measurements have shown[8] that 81.8 kcal/mol are available to N_2 and 2,3-dimethyl-2-butene in the decomposition of 3. Although no similar measurements are available for 2, thermochemical estimates[18] indicate that the exothermicity is not likely to be substantially different. Of all possible mechanisms for energy disposal in a unimolecular reaction, three distinct fates for the reaction exothermicity in 3 might be distinguished in the photoelectron spectrum: formation of triplet 2,3-dimethyl-2-butene,[8] and no vibrational excitation in N_2; vibrational excitation of either the alkene or N_2 fragments; or vibrational excitation in both fragments. Because norbornene decomposes under our conditions, only vibrational excitation of N_2 would be observed in the pyrolysis of 2.

In contrast to the diazetines, 1-pyrazoline 1 is estimated[18] to have only 16 kcal/mol available for distribution among product degrees of freedom. As in the case of 2, only N_2 excitation, if present, would be observable. Nevertheless, if all 16 kcal were available to the N_2 fragment, vibrational excitation would be evident in the photoelectron spectrum (see Appendix).

Examination of Figures 3-5 reveals that vibrational hot bands are not observed for N_2 in these decompositions, indicating that at most $\lesssim$ 5% of the molecules are in the $v = 1$ state. This result poses certain constraints for the reaction dynamics, as follows. The N_2 detected by photoelectron spectroscopy has existed for up to several milliseconds (several thousands of vibrational periods), and suffered up to 100 collisions, most of which are likely to occur with the walls at low pressures. Thus it is expected that the internal energy distribution within the product N_2 molecules will be completely statistical, and characterizable by a vibrational temperature. It is not expected, however, that a significant amount of this internal energy be removed from the N_2 population by collisions.[24-26] As shown in the Appendix, an average value of 0.5 kcal/mol would have to have been released to the nitrogen vibration at the transition state in order for $\gtrsim$ 5% of the N_2 molecules to have one quantum of vibrational energy. This is a lower limit to our detectibility, and hence an upper limit to the energy actually present in the N_2. If the nitrogen were extruded in a concerted fashion, it would be expected to have the same bond length as in the azo compound, i. e., ~ 1.24 Å <u>vs</u> 1.09 Å[27] for a N≡N triple bond. Thomas, Sutin and Steel[28] have estimated on the basis of these bond lengths that N_2 produced in a concerted reaction would be likely to have up to 4 quanta of vibrational energy, or 26.7 kcal/mol. The fact that such high levels of excitation were not observed in the present experiments suggests that the nitrogen is born undistorted in the decomposition of **1**-**3**, and that energy released from the transition states is randomized throughout the products.

This conclusion can be used to predict the expected excitation of N_2 in the decomposition of **3**, providing a check on internal consistency. Highly efficient coupling in the transition state would result in both N_2 and hydrocarbon products having a single vibrational temperature, if it is assumed that all of the reaction exothermicity is released to internal motion, and not rotation or relative translation. Approximately 81 kcal/mol of internal excitation of 2, 3-dimethyl-2-butene corresponds to a vibrational temperature of $\sim$ 780° C (see Appendix). At this temperature, the internal energy of N_2 would be less than 150 cal/mol above zero point energy, well below the 500 cal/mol upper limit determined by experiment.

It is difficult to assess the initial internal energy of the butene fragment generated in the thermolysis of **3**. Special efforts were made to detect the presence of any excitation in the C=C stretching mode. None was observed, with the detection limit being $\leq 3\%$ in this case. As shown in the Appendix, this provides an upper limit of 27 kcal/mol to the internal energy of 2, 3-dimethyl-2-butene at the time of photoionization. However, collisions with the wall prior to detection may have been responsible for removing most of the internal energy initially present in the olefin. Thus no conclusions can be made concerning the distribution of reaction exothermicity among vibrations of the olefin, and rotations and translations of both fragments.

One final possible fate of the exothermicity remains to be explored. It has been suggested[8] that in the decomposition of 3, triplet 2, 3-dimethyl-2-butene might be formed, since the energy in the transition state is slightly higher than various estimated values for the adiabatic transition energy from N → T.[29] No triplet butene was observed in the present work. Studies of the lifetime of triplet cis and trans 2-butene showed that it decays in less than 1 ms, probably by internal conversion to the ground state.[30] Energy transfer to some other species, or to the walls of the pyrolysis region might also have occurred. It is more likely, however, that little, if any, of the triplet was present at any time. An argument supporting this can be made as follows. The adiabatic transition to triplet 2, 3-dimethyl-2-butene requires $\lesssim 76 \pm 2$ kcal/mol as determined by electron impact.[29] The vertical, or most probable, transition requires 94.5 ± 2 kcal/mol. Thus, although there is formally enough energy in the transition state for the olefin to cross over to the triplet surface, the probability for this to occur will be low because of low Franck-Condon overlap between the singlet and triplet states near the transition threshold. Further evidence against triplet formation is provided by recent experiments on a related system, meso- and dl-3, 4-diethyl-3, 4-dimethyldiazetine.[7] The two 3, 4-dimethyl-3-hexene isomers were found to be formed stereospecifically, indicating no twisting about the $C_3{=}C_4$ bond to have occurred during the pyrolysis. If the triplet olefin had been formed, some stereorandomization would probably have taken place.

The fact that essentially none of the reaction exothermicity is being trapped in vibration of the N_2 fragment indicates that there is efficient coupling among internal degrees of freedom of the dissociating molecule as it passes through the transition state. This efficient coupling is not inconsistent with the proposed stepwise mechanism[5] for the decomposition of 1, assuming Bauer's criterion[1] to be applicable. It is not clear, however, whether such a mechanism would have been expected in the case of 2 and 3. Recent studies of a diazetine decomposition[7] indicate that, if the bond cleavage is stepwise, the intermediate diazenyl biradical has a lifetime shorter than the time required for rotation about the C–C bond. This timescale does not allow differentiation to be made between a concerted and a stepwise mechanism. If the mechanism is stepwise, then the present experiments are consistent with the predictions of Bauer. If it is a concerted [2s + 2a] elimination, however, then Bauer's criterion is not upheld, and the dynamics expected from concerted and nonconcerted reactions should be reinvestigated.

The results of the present work can be used to examine a study by Shen and Bergman.[31] Both symmetric and unsymmetrically substituted 1-pyrazolines were thermally decomposed, and labelling studies performed to determine the extent of vibrational excitation in the newly-formed hydrocarbon fragment. It was found that the symmetric pyrazoline yielded a much colder organic moeity than the unsymmetric one. This observation was rationalized in terms of Bauer's criterion. The symmetric pyrazoline decomposed by a concerted process to give vibrationally excited N_2 while the unsymmetric one fragmented in a stepwise fashion wherein the organic product retained a great deal of internal energy. It was suggested that symmetrically substituted cyclic azo compounds in general would be the most likely systems to give rise to vibrationally excited N_2. It appears from the present results that the requirement of symmetrical substitution is not stringent enough. Their observations of two different levels of excitation in the organic fragment is very interesting, however, and experiments involving the same pyrazolines will be performed in our laboratory to determine whether the predicted presence of vibrationally excited N_2 is borne out. These experiments will provide a good test of the applicability of Bauer's criterion to the thermolysis of azo compounds.

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Appendix

In order to estimate limits for the extent of energy disposal into product vibrations during the decomposition of azo compounds, approximate total vibrational energies were calculated for each product as a function of temperature. Several assumptions were made in the calculations.

(i) The azo compounds were at equilibrium initially, with a temperature of 298° K.

(ii) On entering the pyrolysis region, the molecules were heated just enough to decompose, and the products formed were not heated further by wall collisions. Thus, the vibrational temperature of the products would be determined by the energy acquired during the unimolecular decomposition alone.

(iii) Collisions and intramolecular V–V coupling would serve only to establish a Boltzmann equilibrium among product vibrational degrees of freedom. This equilibrium is characterizable by a temperature.

Thus, the vibrational energy-vibrational temperature curves apply only in the absence of energy removal by V–R, T transfer mechanisms.

The expression used in the calculations is

$$E_{tot}(T) = \sum_{v=1} \sum_{n=1} E_{nv} g_v e^{-E_{nv}/RT} \qquad (1)$$

where E_{nv} is the energy of the nth level of the vth vibrational mode, g_v is the degeneracy of that mode, and E_{tot} is the total vibrational energy at a particular temperature T in kcal/mol. Zero-point energy is not included. 2, 3-Dimethyl-2-butene has 48 normal modes, not all of which have been observed.[22, 32, 33] The seven modes that were missing were assigned frequencies over a range of 1000-400 cm^{-1}. Then the modes were grouped such that all those having an energy in a 100 cm^{-1} range were given an energy equal to their average, to be multiplied by the appropriate degeneracy g_v. This reduced the number of sums over v from 48 to 19. The frequency used for N_2 was taken from Herzberg.[34] The results of the calculations are shown in Figure 6, and some excited state populations given in Table I. The errors associated with the calculated curves arise from truncation of sums for both fragments, and simplification of the vibrational spectrum for 2, 3-dimethyl-2-butene. The magnitude of the error is difficult to assess. For N_2 it is $\leq 2\%$, and, for the olefin, a more conservative value of 5%.

FIGURE 6

Total vibrational energy content as a function of temperature in 2, 3-dimethyl-2-butene and nitrogen.

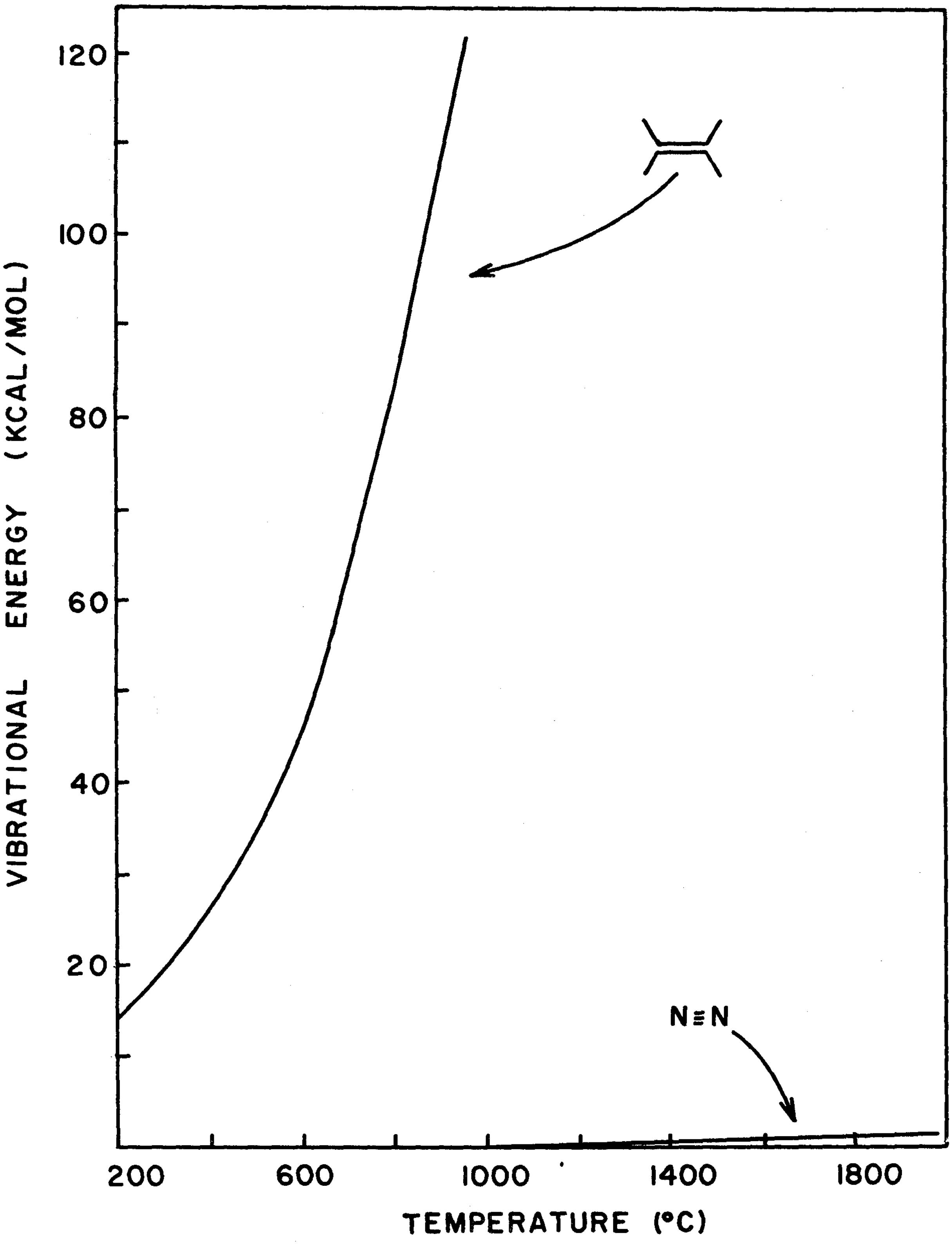
120
100
80
60
40
20
VIBRATIONAL ENERGY (KCAL/MOL)
200
600
1000
1400
1800
TEMPERATURE (°C)
N≡N

TABLE I: Levels of Vibrational Excitation in Specific Modes at Selected Temperatures

Vibrational Temperature (° C)	Population of v = 1 level: N_1/N_0	
	N_2 stretch	2, 3-dimethyl-2-butene $C_2{=}C_3$ stretch
400	0.007	0.028
500	0.013	0.044
600	0.022	0.063
700	0.032	0.084
800	0.044	0.106
900	0.057	0.128
1000	0.072	0.151
1500	0.151	0.257

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