7336 J. Am. Chem. Soc. 1984, 106, 7336–7347

$V^M(r)$ is taken as function of the coordinates to permit a fast evaluation of it and of its first and second derivatives. $V_\sigma(r)$ includes contributions from bonding, bond angle, torsion angle, and nonbond interaction terms and is introduced as an analytical function of the coordinates,

$$\begin{aligned}\mathrm{V}_\sigma(r) = {}& \tfrac{1}{2}\sum_i D_b[\exp(-2a(b - b_\mathrm{o})) - 2\exp(-a(b - b_\mathrm{o}))] + \\ & \tfrac{1}{2}\sum_i K_\theta(\theta_i - \theta_\mathrm{o})^2 + \tfrac{1}{2}\sum_i K_x(x_i - x_\mathrm{o})^2 + \tfrac{1}{2}\sum_i F(q_i - q_\mathrm{o})^2 + \\ & \tfrac{1}{2}\sum_i K_\phi^{(1)}\cos\phi_i + \tfrac{1}{2}\sum_i K_\phi^{(2)}\cos 2\phi_i + \\ & \tfrac{1}{2}\sum_i K_{\theta\theta'}(\theta_i - \theta_\mathrm{o})(\theta'_i - \theta_\mathrm{o})\cos\phi_i + \sum_{ij}[A\exp(-\mu r_{ij}) - Br_{ij}^{-6}]\end{aligned}$$

where b_i are bond distances, θ_i are bond angles, ϕ_i are torsion angles, q_i are 1–3 nonbonded distances, r_{ij} are all higher order nonbond distances, and x are out of plane angles. D, a, b, K_θ, θ_o, F, q, K_x, K_ϕ, $K_{\phi'}$, $K_{\theta\theta'}$, A, B, and μ are adjustable parameters which depend on the type of atoms involved.

The π-potential term, corrected for nearest-neighbor orbital overlap is

$$\begin{aligned}V_\pi{}^\circ(r) = {}& \sum_\mu P_{\mu\mu}(r)[{}^\lambda W_\mu(r)P_{\mu\mu}(r){}^\lambda\gamma_{\mu\mu}(r) + \tfrac{1}{4}P_{\mu\mu}(r){}^\lambda\gamma_{\mu\mu}(r)] + \\ & 2\sum_{\mu<\nu} P_{\mu\nu}(r){}^\lambda\beta_{\mu\nu}(r) - \sum_{\mu<\nu}[\tfrac{1}{2}P_{\mu\nu}{}^2(r) - Q_\mu(r)Q_\nu(r){}^\lambda\gamma_{\mu\nu}]\end{aligned}$$

where $P_{\mu\mu}$ is the π-electron density on the μth atom, $P_{\mu\nu}$ is the π-bond order between atoms μ and ν, ${}^\lambda W_\mu$ and ${}^\lambda\beta_{\mu\nu}$ are the core integrals, ${}^\lambda\gamma_{\mu\mu}$ is the Coulomb integral for the μth atom, and ${}^\lambda\gamma_{\mu\nu}$ is the interchange integral for atoms μ and ν, all corrected for nearest-neighbor orbital overlap. Q_μ are the atomic charges.

$V_\pi{}^\circ(r)$ is set in analytical form in terms of zero order π-functions and its dependence on the geometry of the system, to introduce the appropriate adjustable parameters:

$${}^\lambda W_\mu = W_{2\mathrm{p}}{}^\circ + \beta'[\exp(-2\mu_\beta(b_{\mu,\mu+1} - b_\mathrm{o}{}^1))\cos^2 t_{\mu,\mu+1}]$$

$$\begin{aligned}{}^\lambda\beta_{\mu,\mu\pm1} = {}& \beta_\mathrm{o}\exp(-\mu_\beta(b_{\mu,\mu\pm1} - b_\mathrm{o}{}^1))(1 + K_\beta(b_{\mu,\mu\pm1} - \\ & b_\mathrm{o}{}^1))\cos(t_{\mu,\mu\pm1})(1 - E_tP_{\mu,\mu\pm1}\cos(t_{\mu,\mu\pm1}))/(1 - E_tP_{\mu,\mu\pm1})\end{aligned}$$

$${}^\lambda\gamma_{\mu,\mu} = (I - A) + G_s[\exp(-2\mu_\beta(b_{\mu,\mu\pm1} - \mathrm{b}_\mathrm{o}{}^1))\cos^2(t_{\mu,\mu\pm1})]$$

$${}^\lambda\gamma_{\mu,\nu} = G'\exp(-\mu_\gamma r_{\mu,\nu}) + e^2/(D + r_{\mu,\nu})$$

where $t = {}^1/_2(\phi_1 + \phi_2 + \phi_3 + \phi_4)$, with ϕ_i the torsional dihedral angles of the conjugated bond and $r_{\mu,\nu}$ the distance between atoms μ and ν.

The excitation energy $\Delta V_\pi{}^M$ is given by

$$\Delta V_\pi{}^M(r) = \sum_\nu R_\nu{}^{W\,\lambda}W_\nu(r) + \sum_\nu R_{\nu\nu}{}^{\gamma\,\lambda}\gamma_{\nu\nu}(r) + \sum_{\nu<\mu} R_{\mu\nu}{}^{\beta\,\lambda}\beta_{\mu\nu}(r) + \sum_{\nu<\mu} R_{\mu\nu}{}^{\gamma\,\lambda}\gamma_{\mu\nu}(r)$$

with $\mathrm{R}_\nu{}^W$, $\mathrm{R}_{\nu\nu}{}^\gamma$, $\mathrm{R}_{\mu\nu}{}^\beta$, and $R_{\mu\nu}{}^\gamma$ excitation coefficients.

With this expression for $V^M(r)$, the equilibrium geometry is found and the mass scaled Cartesian origin shift

$$\Delta^M = M^{-1/2}(r_\mathrm{eq}{}^M - r_\mathrm{eq}{}^G)$$

with M a diagonal matrix of the atomic masses, is evaluated. The complete set of vibrational frequencies ν and the normal coordinates vectors **L** can be evaluated by diagonalizing the matrix of mass scaled Cartesian second derivatives of $V^M(r)$ at the calculated minimum. In this way it is possible to identify each Raman frequency with its normal vibrational mode. The relative intensities are proportional to the Franck–Condon factors.

Registry No. I, 10035-62-8; II, 92219-97-1; III, 92219-98-2; IV, 68996-06-5; VII, 88471-57-2.

Photoelectron Spectroscopy of Isomeric C_4H_7 Radicals. Implications for the Thermochemistry and Structures of the Radicals and Their Corresponding Carbonium Ions

Jocelyn C. Schultz, F. A. Houle, and J. L. Beauchamp*

Contribution No. 6699 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. *Received December 27, 1983*

Abstract: The first photoelectron bands of 1-methylallyl, 2-methylallyl, allylcarbinyl, and cyclobutyl radicals have been obtained. Adiabatic and vertical ionization potentials respectively are 7.49 ± 0.02 and 7.67 ± 0.02 eV for the 1-methylallyl radical, 7.90 ± 0.02 and 7.95 ± 0.02 eV for the 2-methylallyl radical, 8.04 (+0.03, −0.1) and 8.47 ± 0.05 eV for the allylcarbinyl radical, and 7.54 ± 0.02 and 7.66 ± 0.02 eV for the cyclobutyl radical. With use of known or estimated radical heats of formation, heats of formation of the corresponding carbonium ions are calculated to be 203.1 ± 1.4 kcal/mol for the 1-methylallyl cation, 212.2 ± 1.6 kcal/mol for the 2-methylallyl cation, 231.0 ± 3 kcal/mol for the allylcarbinyl cation, and 225.1 ± 1.1 kcal/mol for the cyclobutyl cation. Vibrational progressions of 990 ± 100 and 410 ± 30 cm^{-1} are resolved on the first photoelectron bands of the cyclobutyl radical and the 2-methylallyl radical, respectively. Vibrational structure is observed on the 1-methylallyl radical photoelectron band, but vibrational progressions could not be assigned. The complex spectrum probably results mainly from the fact that it is ascribed to two isomers, *cis*- and *trans*-1-methylallyl radicals. The presence of vibrational structure on the first photoelectron bands of these radicals is consistent with the ions being at local minima on the $C_4H_7^+$ potential surface. Major thermal decomposition and isomerization products of 1-methylallyl, 2-methylallyl, allylcarbinyl, cyclobutyl, and cyclopropylcarbinyl radicals are identified in the photoelectron spectra. No thermolysis products of the 2-methylallyl radical are observed. A small amount of 1,3-butadiene and/or 2-butene is observed at high temperatures from the 1-methylallyl radical. Pyrolysis of the allylcarbinyl radical yields the 1-methylallyl radical and 1,3-butadiene. Due to its facile ring opening to the allylcarbinyl radical (which is observed along with its thermolysis products), the cyclopropylcarbinyl radical itself is not observed. Pyrolysis of the cyclobutyl radical yields 1-methylallyl and 1,3-butadiene. The allylcarbinyl radical, the direct product of the cyclobutyl radical ring opening, is not observed, presumably because it is formed with sufficiently high internal energy to further rearrange rapidly.

In solution, numerous experiments have been performed to gather structural, spectroscopic, and kinetic data on $C_4H_7^+$ under stable ion and solvolytic conditions in order to characterize the intermediate(s) involved in the cyclopropylcarbinyl, cyclobutyl,

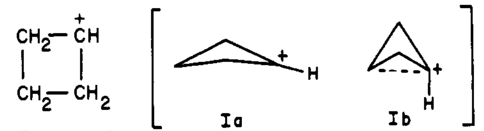
0002-7863/84/1506-7336$01.50/0

and allylcarbinyl interconversions.[1-3] Relatively few experiments have been performed to characterize the gas-phase $C_4H_7^+$ species.[4-8] Structural identities, corresponding heats of formation, and interconversion pathways of the $C_4H_7^+$ species in the gas phase are not well established.

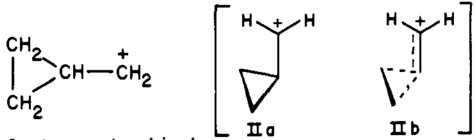
Since photoelectron band shapes are governed by Franck–Condon factors, the photoelectron spectrum of a radical[9] provides information about the ionic potential surface in the region where the geometry most closely resembles that of the radical. In the present study, the appropriate nitrite precursors have been decomposed to yield cyclobutyl, allylcarbinyl, 1-methylallyl, and 2-methylallyl radicals. These radicals have been well studied by ESR spectroscopy, yielding structural information, and their thermochemistry is known or can be estimated. The first bands in the photoelectron spectra of these C_4H_7 radicals are analyzed in this study, in conjunction with the ESR and thermochemical data for the radicals, to obtain accurate thermochemical and at least qualitative structural data for the gas-phase cyclobutyl cation (I), allylcarbinyl cation (III), 1-methylallyl cation (V), and 2-methylallyl cation (VI).

The extensive experimental evidence on $C_4H_7^+$ in condensed media indicates that the solution-phase species prepared from cyclobutyl or cyclopropylcarbinyl derivatives may not be represented by one static structure. Controversy continues regarding the structures involved in the equilibrium. Rapidly interconverting equivalent classical (IIa) or nonclassical (IIb) bisected cyclopropylcarbinyl cations or equivalent bicyclobutonium cations (IV) have all been proposed. Puckered cyclobutyl cation (Ib) has been postulated as the intermediate or transition state through which equivalent structures equilibrate. Recent NMR experiments under stable-ion conditions indicate the major, most stable species has the bicyclobutonium structure,[2c,e] and the bisected cyclopropylcarbinyl structure can be assigned to a minor species of very similar stability.[2c] An unsuccessful attempt has been made to determine whether cyclopropylcarbinyl cation or 1-methylallyl cation (V), which can be prepared from 1-methylallyl derivatives, is thermodynamically more stable in solution.[3]

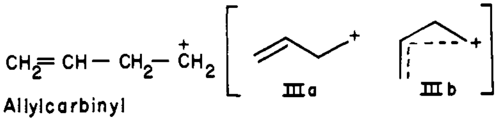
In the gas phase, fragment ion thresholds from hydrocarbons often correspond to formation of the most stable isomer, even when extensive rearrangements are required.[10] Ionic heats of formation corresponding to appearance potentials for $C_4H_7^+$ from many alkanes and alkenes are very close, implying that the $C_4H_7^+$ fragment formed has a common structure.[4] Taking into account a presumed kinetic shift in the appearance potential, the heat of formation of this $C_4H_7^+$ fragment ion coincides with that of 1-methylallyl cation determined by ionization of 1-methylallyl radical. Ionization potentials of three C_4H_7 radicals, determined by electron impact,[4,5] can be combined with the heats of formation of the radicals[11] to order the $C_4H_7^+$ cations according to increasing heats of formation: 1-methylallyl, 2-methylallyl, and cyclobutyl cation.



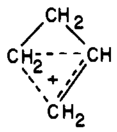
I Cyclobutyl



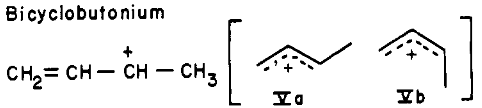
II Cyclopropylcarbinyl



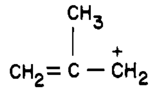
III Allylcarbinyl



IV Bicyclobutonium



V 1-Methylallyl



VI 2-Methylallyl

Some experiments have been done in the gas phase to determine the stable $C_4H_7^+$ species and to study the interconversion of isomers. Measurements of the kinetic energy released when five isomers of $(C_4H_7Br)^+$ lose Br to form $C_4H_7^+$ indicate that cyclopropylcarbinyl and allylcarbinyl cations can rearrange with little activation energy to a more stable species. In contrast, cyclobutyl cation and 1- and 2-methylallyl cations exist in potential wells in the gas phase.[6] In elegant radiochemical experiments, β-decay by cyclobutane $C_4H_{7-n}T_{n+1}$ yields $C_4H_{7-n}T_n^+$ cations which react with a nucleophile to yield cyclobutyl and cyclopropylcarbinyl products, indicating that gas-phase cyclobutyl cations exist for at least 10^{-9} s in a cyclic structure.[7] A different multistep trapping technique has been used to identify the $C_4H_7^+$ ions formed by fragmentation of protonated cyclopropylcarbinol and bromocyclobutane.[8] After neutralization of the ions by electron capture, the ensuing radicals are trapped in a fast reaction with a neutral. The products of this reaction, after ionization by electron capture, are analyzed by using mass selected collisional mass spectroscopy. The results of these experiments indicate that an identical mixture of $C_4H_7^+$ ions was formed during the time before their neutralization ($\sim 10^{-5}$–10^{-4} s), regardless of whether the initial ions had the cyclobutyl or cyclopropylcarbinyl structure. This mixture consisted of 36 ± 10% cyclobutyl, 47 ± 10% allylcarbinyl or cyclopropylcarbinyl, and 17 ± 10% tertiary methylcyclopropyl or secondary allyl ions.

Various theoretical approaches have been used to predict the relative stabilities of the $C_4H_7^+$ cation intermediates.[12,13] Recent 4-31G ab initio molecular orbital calculations have determined that bisected cyclopropylcarbinyl cation (IIa) and a structure

---

(1) Reviews: (a) Richey, G. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 25. (b) Wiberg, K. B.; Hess, B. A.; Ashe, A. J. In ref 1a, Chapter 26. (c) Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; Chapter 5.

(2) Recent investigations: (a) Olah, G. A.; Jeuell, C. L.; Kelley, D. P.; Porter, R. D. *J. Am. Chem. Soc.* **1972**, *94*, 146. (b) Kelley, D. P.; Underwood, G. R.; Barron, P. F. *Ibid.* **1976**, *98*, 3106. (c) Staral, J. S.; Yavari, I.; Roberts, J. D.; Prakash, G. K. S.; Donovon, D. J.; Olah, G. A. *Ibid.* **1978**, *100*, 8016. (d) Staral, J. S.; Roberts, J. D. *Ibid.*, **1978**, *100*, 8018. (e) Saunders, M.; Siehl, H. U. *Ibid.* **1980**, *102*, 6868.

(3) Mayr, H.; Olah, G. A. *J. Am. Chem. Soc.* **1977**, *99*, 510.

(4) Lossing, F. P. *Can. J. Chem.* **1972**, *50*, 3973.

(5) (a) Pottie, R. F.; Harrison, A. G.; Lossing, F. P. *J. Am. Chem. Soc.* **1961**, *83*, 3204. (b) Lossing believed the radical identified as the cyclobutyl radical may have isomerized to 2-methylallyl. Reference 37, p 127.

(6) Bowen, R. D.; Williams, D. H.; Schwarz, H.; Wesdemiotis, C. *J. Chem. Soc., Chem. Commun.* **1979**, 261.

(7) Cacace, F.; Speranza, M. *J. Am. Chem. Soc.* **1979**, *101*, 1587.

(8) McEwen, C. N.; Rudat, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 4355.

(9) For related works see: (a) Dyke, J. M.; Jonathan, N.; Morris, A. *Int. Rev. Phys. Chem.* **1982**, *2*, 3. (b) Dewar, M. J. S.; David, D. E. *J. Am. Chem. Soc.* **1980**, *102*, 7387. (c) Koenig, T.; Chang, J. C. *Ibid.* **1978**, *100*, 2240.

(10) Lossing, F. P.; Traeger, J. C. *Int. J. Mass. Spectrom. Ion. Phys.* **1976**, *19*, 9.

(11) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(12) Radom, L.; Poppinger, D.; Haddon, R. C. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1976; Vol. V, Chapter 38.

(13) (a) Hehre, W. J.; Hiberty, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 302. (b) Hehre, W. J.; Hiberty, P. C. *Ibid.* **1972**, *94*, 5917. (c) Levi, B. A.; Blurock, E. S.; Hehre, W. J. *Ibid.* **1979**, *101*, 5537. (d) Hehre, W. J., private communication.

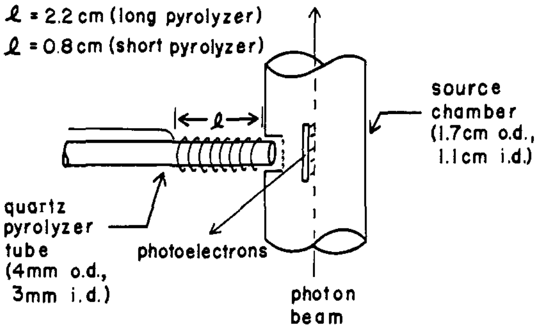


Figure 1. Schematic of the pyrolyzer and photoionization region.

coinciding approximately to formulations for bicyclobutonium ion (IV) are at local minima on the $C_4H_7^+$ potential surface; puckered cyclobutyl cation (Ib) collapses without barrier to bisected cyclopropylcarbinyl cation.[13c] At the STO-3G level, allylcarbinyl cation (IIIa and IIIb) also collapses without barrier to bisected cyclopropylcarbinyl cation.[13b] No local minimum corresponding to cyclobutyl cation with a less puckered ring and a more planar cation center (Ia) was found, this species being higher in energy than puckered cyclobutyl cation.[13d]

As yet there is no consistent picture of the $C_4H_7^+$ system in the gas phase. For example, theory has failed to find a local minimum corresponding to cyclobutyl cation, but experiments seem to indicate it is a stable gas-phase species. A bicyclobutonium ion has been found by theory to be at a local minimum, but without gas-phase spectroscopic information on the ions, the results of trapping experiments are interpreted only in terms of classical ion structures. Condensed-phase results cannot automatically by applied to the gas phase. The effects on structures and energies of carbonium ions in going from the gas phase into stable-ion media have been studied.[14] Differences in solvation among carbonium ion isomers and rearrangement transition states appear to be small. However, some evidence indicates that the largest differences occur when there are significant changes in the extent of charge delocalization in the cation. Thus, the $C_4H_7^+$ system should provide an interesting test of differential solvation effects. In the present study we report C_4H_7 radical photoelectron spectra which provide structural and thermochemical information about several gas-phase $C_4H_7^+$ isomers. Our analysis of the data indicates these isomers have structures corresponding most closely to slightly puckered cyclobutyl cation (Ia), primary allylcarbinyl cation (IIIa), 1-methylallyl cation (Va and Vb), and 2-methylallyl cation (VI). In addition, thermal decomposition and isomerization products of 1- and 2-methylallyl, allylcarbinyl, cyclobutyl, and cyclopropylcarbinyl radicals are identified in the photoelectron spectra. Cyclopropylcarbinyl radical itself is not observed, due to its facile ring-opening isomerization to allylcarbinyl radical.

Experimental Section

Photoelectron spectra were recorded on a spectrometer of standard design, which has been modified for the study of the products of gas-phase pyrolysis. A detailed description has been given elsewhere.[15] A schematic of the pyrolysis and photoionization regions is shown in Figure 1. Pyrolysis takes place in a quartz tube, the end of which is wrapped with double-stranded, insulated heating wire. A thermocouple (not shown in Figure 1) is wedged between the wire and the quartz tube to monitor the temperature. The tip of the tube is inserted into an aperture in the source chamber. The photon beam is directed along the axis of the cyclindrical source chamber. Photoelectrons ejected perpendicular to the quartz tube and the photon beam are energy analyzed. Most of the experiments were done with use of a long pyrolyzer (l = 2.2 cm) at temperatures from 500 to 700 °C. Since the pyrolysis is done at low pressures (~10^{-2} torr), molecules are heated mainly by collisions with the wall of the pyrolyzer, and there are fewer molecule–molecule collisions. During the ~1-ms residence time of a molecule in the long pyrolyzer, it experiences ~150 collisions with the wall, and ~50 collisions with other molecules. Unimolecular radical processes result primarily from activation on the pyrolyzer wall and may, in fact, occur while the molecule is in contact with the surface. In an attempt to increase the concentration of the initial radical formed by decreasing the radical pyrolysis products, a short pyrolyzer (l = 0.8 cm) was used for some experiments. Pyrolysis temperatures from ~80 to 130 °C higher were necessary with the shorter pyrolyzer to obtain the same amount of precursor decomposition achieved with the long pyrolyzer. Spectra showing the same amount of precursor decomposition were compared, and no increase of the primary radical products nor decrease in the secondary radical products, compared to the amount of nitrite decomposition, was apparent. Furthermore, there is no evidence that the slightly higher pyrolysis temperatures change the shapes of the radical spectra (due to a temperature-dependent population of radical conformations or higher vibrational states) and in particular no hot bands were observed. We choose to report the best spectra obtained with both pyrolyzers.

Radicals were produced by pyrolysis of alkyl nitrites, reactions 1 and 2, where R = 1-methylallyl, 2-methylallyl, allylcarbinyl, cyclobutyl, and cyclopropylcarbinyl. The nitrites were prepared from the corresponding

$$RCH_2ONO \rightarrow RCH_2O + NO \tag{1}$$

$$RCH_2O \rightarrow R + CH_2O \tag{2}$$

alcohols with use of standard techniques.[16] 2-Methyl-3-buten-1-ol was obtained from Chemical Samples Co., 3-methyl-3-buten-1-ol from Chemical Dynamics Corp., and cyclobutanemethanol and 4-penten-1-ol from Aldrich. 2-Cyclopropylethanol was prepared from cyclopropyl bromide (Aldrich). Cyclopropyl bromide was reacted with finely divided lithium in diethyl ether, giving a solution of cyclopropyllithium.[17] 2-Cyclopropylethanol was then obtained by reacting this solution with ethylene oxide.[18] The alcohol was purified by gas-phase chromatography. To produce separately the cis and trans isomers of 1-methylallyl radical as the initial pyrolysis products, *cis*- and *trans*-3-penten-1-ol were used to make the nitrite precursor. To prepare *cis*-3-penten-1-ol, pent-3-yn-1-ol (Farchan) was hydrogenated at room temperature and atmospheric pressure in the presence of a palladium–calcium carbonate catalyst and with ethyl acetate as solvent.[19] To prepare *trans*-3-penten-1-ol, pent-3-yn-1-ol was reacted with sodium in liquid ammonia under argon atmosphere and the reaction was quenched with ammonium chloride.[20] Purified products were analyzed by capillary gas chromatography (SE-30 column at 60 °C). The *cis*-3-penten-1-ol was >95% pure, the major impurity being pent-3-yn-1-ol. The *trans*-3-penten-1-ol was 99% pure. The nitrites prepared from these alcohols were also analyzed and found to be 90% pure, the major impurity being the alcohols with <2% of the other nitrite isomer.

Alkyl nitrites have an activation energy of ~40 kcal/mol toward decomposition to NO and alkoxy radicals (reaction 1).[21] Alkoxy radicals are quite unstable thermally. For example, the activation energy for decomposition of C_2H_5O to CH_3 and CH_2O is 21.6 kcal/mol.[21] The intermediate alkoxy radicals have never been observed in these experiments, but since their ionization potentials are expected to be ~9.2 eV,[22] their spectra would be at least partially obscured by precursor and product photoelectron spectra.

The activation energy for alkyl nitrite decomposition is comparable to activation energies for decomposition or isomerization of the initial alkyl radicals produced by nitrite decomposition. Thus, in one spectrum, undecomposed nitrite, the initial alkyl radical, and products from unimolecular and possibly wall reactions of this radical can be identified. By changing the pyrolysis temperature, the extent of radical decomposition present in the spectrum can be varied.

When necessary, spectra were recorded with use of both He I and Ne I radiation in order to determine those spectral features arising from He Iβ ionization. Energy scales were calibrated by using the peaks due to CH_2O, NO, Ar, and 1,3-butadiene. CH_2O and NO result from the nitrite decomposition. The first two peaks of the butadiene photoelectron spectrum nearly coincide with the He Iβ line of CH_2O and the first NO peak. They were used for calibration purposes when butadiene appeared as a major decomposition product and its spectrum was the dominant feature in the 9.0–9.5 eV spectral region. Spectra of authentic samples

---

[14] Saunders, M.; Chandrasekhar, J.; Schleyer, P. v. R. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. I, Essay 1.

[15] Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3290.

[16] Levin, N.; Hartung, W. "Organic Synthesis"; Wiley: New York, 1955; Collect. Vol. III, 192.

[17] Seyferth, D.; Cohen, H. M. *J. Organomet. Chem.* **1963**, *1*, 15.

[18] Hart, H.; Wyman, D. P. *J. Am. Chem. Soc.* **1959**, *81*, 4891.

[19] Crombie, L.; Harper, S. H. *J. Chem. Soc.* **1950**, 873.

[20] Sondheimer, F. *J. Chem. Soc.* **1950**, 877.

[21] Batt, L. *Int. J. Chem. Kinet.* **1979**, *11*, 977.

[22] Williams, J. M.; Hamill, W. H. *J. Chem. Phys.* **1968**, *49*, 4467.

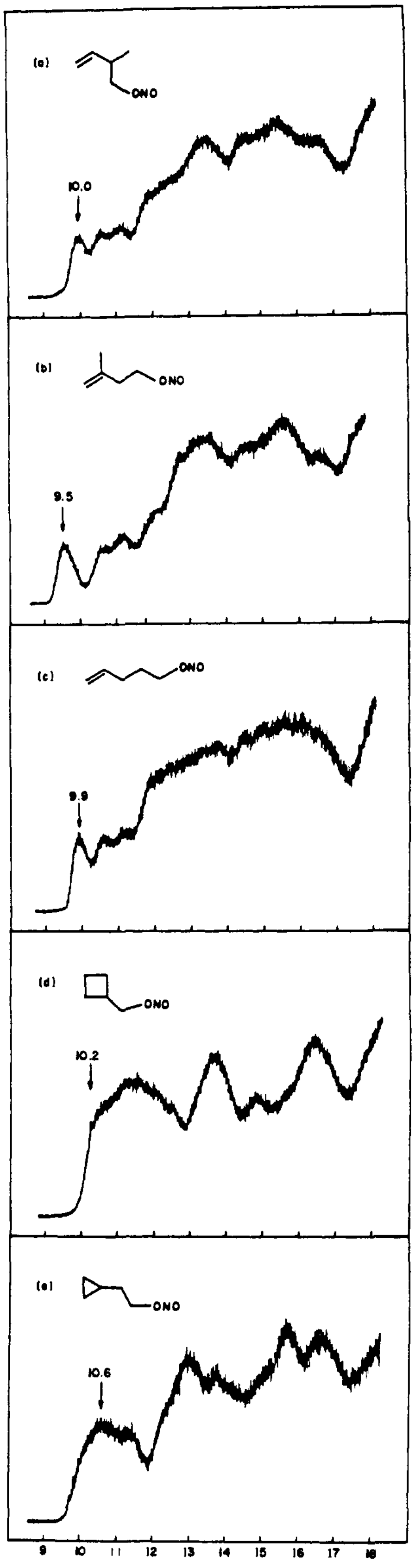


Figure 2. He I spectra of (a) 2-methyl-3-buten-1-yl nitrite, (b) 3-methyl-3-buten-1-yl nitrite, (c) penten-1-yl nitrite, (d) cyclobutylmethyl nitrite and (e) 2-cyclopropylethyl nitrite.

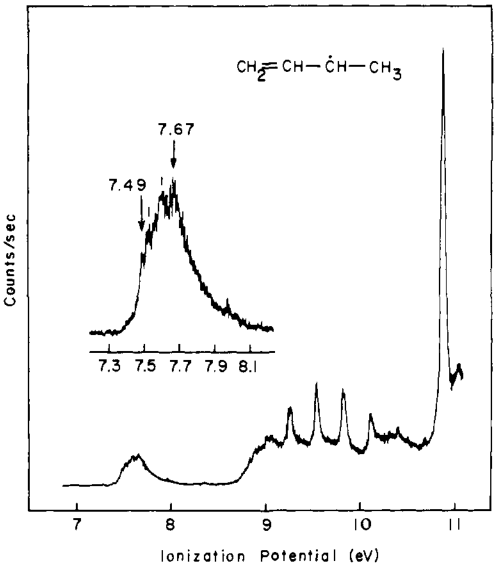


Figure 3. He I spectrum of 1-methylallyl radical. Other pyrolysis products of 2-methyl-3-buten-1-yl nitrite are observed. Peaks at 9.2–10.1 and 10.884 eV are fromNO and CH_2O, respectively. The peak at 9.0 eV is due to He Iβ ionization of CH_2O and some 1,3-butadiene and/or 2-butene. The insert shows the 1-methylallyl radical band in greater detail.

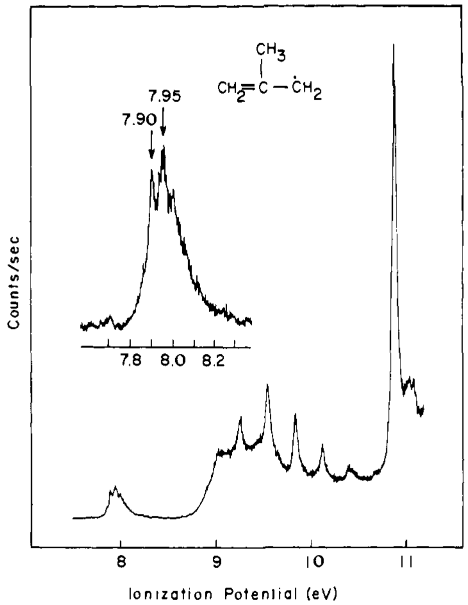


Figure 4. He I spectrum of 2-methylallyl radical. Other observed pyrolysis products of the 2-methylallyl radical nitrite precursor are NO and CH_2O. The insert shows the 2-methylallyl radical band in greater detail.

Table I. C_4H_7 Radical Photoelectron Data

radical	ionization potential, eV		vibrational structure, cm^{-1}
	adiabatic	vertical	
1-methylallyl	7.49 ± 0.02	7.67 ± 0.02	observed
2-methylallyl	7.90 ± 0.02	7.95 ± 0.02	410 ± 30
allylcarbinyl	8.04 (+0.03, -0.1)	8.47 ± 0.05	none observed
cyclobutyl	7.54 ± 0.02	7.66 ± 0.02	990 ± 100

of 1-butene, *cis*- and *trans*-2-butene, and 1,3-butadiene were recorded in our laboratory and used along with published adiabatic ionization potentials of these molecules[23,24] for comparison with nitrite pyrolysis spectra. Resolution for these experiments was approximately 30–40 mV. Reported ionization potentials are the average of several determinations. Error limits indicate the reproducibility of the numbers, except for the ionization potentials of allylcarbinyl radical where circumstances de-

---

[23] Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213.

[24] Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. "Molecular Photoelectron Spectroscopy"; Wiley-Interscience: London, U.K., 1970.

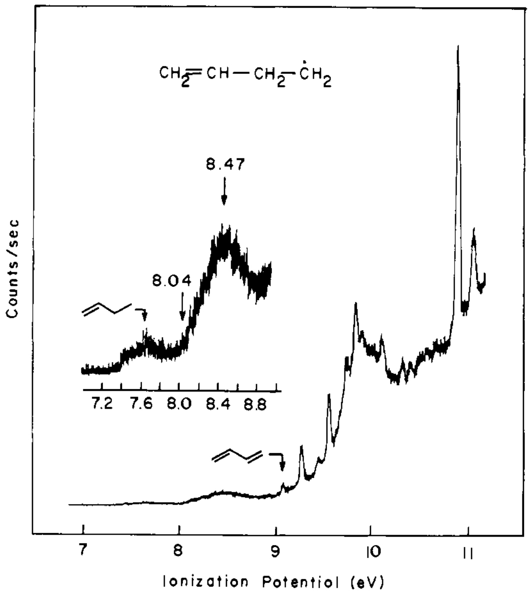


Figure 5. Ne I spectrum of allylcarbinyl radical. The 1-Methylallyl radical (7.4–8.0 eV), 1,3-butadiene, NO, and CH_2O are also observed as pyrolysis products of the allylcarbinyl radical nitrite precursor. The insert shows the allylcarbinyl radical band in greater detail.

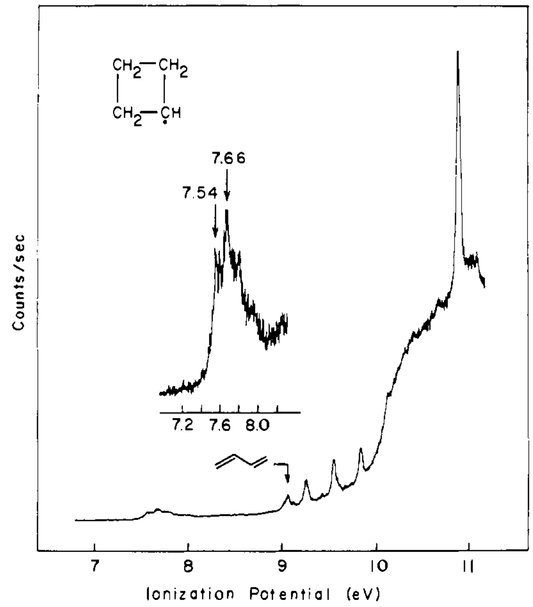


Figure 6. He I spectrum of cyclobutyl radical. NO, CH_2O, and 1,3-butadiene are also observed as pyrolysis products of the cyclobutyl radical nitrite precursor. The insert shows the cyclobutyl radical band in greater detail.

scribed below required larger error limits.

Results

Spectra obtained in these experiments are presented in Figures 2–8. The C_4H_7 radical photoelectron data are summarized in Table I. Spectra of the initial alkyl radical products and the results of their decomposition or isomerization were identified by considering the temperature-dependent nitrite thermolysis spectra together with thermal decomposition mechanisms for C_4H_7 radicals reported in the literature and published spectra or spectra taken in our laboratory of possible decomposition products.

Nitrites. The photoelectron spectra of 2-methyl-3-buten-1-yl nitrite, 3-methyl-3-buten-1-yl nitrite, 4-penten-1-yl nitrite, cyclobutanemethyl nitrite, and 2-cyclopropanethyl nitrite are presented in Figure 2. The vertical ionization potentials (IPs) of these species are approximately 10.0, 9.5, 9.9, 10.2, and 10.6 eV, respectively.

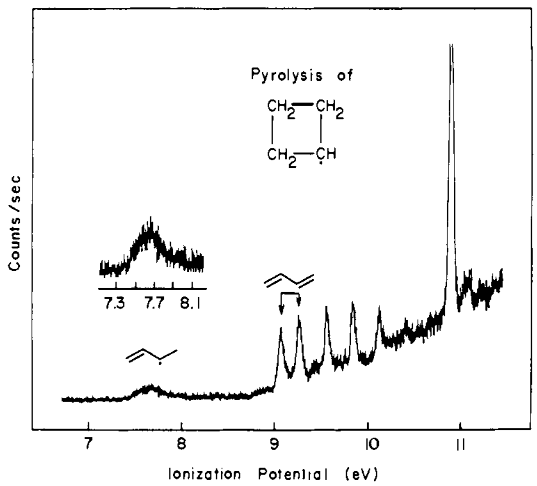


Figure 7. He I spectrum of high-temperature pyrolysis products of the cyclobutyl radical precursor. The band at 7.4–7.9 eV is primarily due to 1-methylallyl radical. NO, CH_2O, and 1,3-butadiene are also present. The peak at 9.26 eV is due to both 1,3-butadiene and NO.

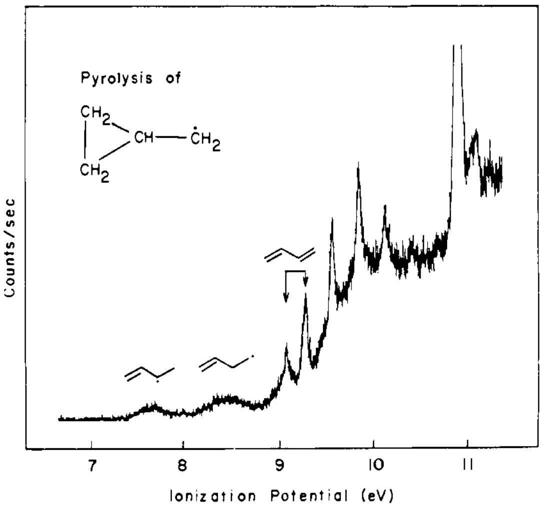


Figure 8. He I spectrum of pyrolysis products of the cyclopropylcarbinyl radical nitrite precursor. The 1-methylallyl radical, the allylcarbinyl radical, 1,3-butadiene, NO, and CH_2O are present. The peak at 9.26 eV is due to both 1,3-butadiene and NO.

1-Methylallyl Radical. A spectrum of the pyrolysis products of the 2-methyl-3-buten-1-yl nitrite precursor to 1-methylallyl radical, recorded with He I radiation and using the short pyrolyzer at 740 °C, is shown in Figure 3. This precursor would be expected to yield some mixture of *cis*- and *trans*-1-methylallyl radicals. Maximum count rates on the 1-methylallyl radical band were ~70 s^{-1}. Vibrational fine structure is resolved on this band, and the prominent features are indicated in the figure inset. However, vibrational progressions could not be assigned. The adiabatic IP was chosen as the first peak of the vibrational fine structure, at 7.49 ± 0.02 eV, and the vertical IP as the most intense feature, at 7.67 ± 0.02 eV. The observed adiabatic and vertical IPs would be expected to depend on the isomeric composition of the 1-methylallyl radical population. A previous determination by electron impact yielded an ionization potential of 7.54 ± 0.05 eV for 1-methylallyl radical.[4]

In an attempt to obtain separate photoelectron spectra of the cis and trans isomers of 1-methylallyl radical, precursors which produce only one of the isomers as their initial pyrolysis product were pyrolyzed at a low temperature (490 °C with the long pyrolyzer). No difference between the 1-methylallyl radical spectrum from the cis, trans, and nonspecific isomer precursors, *cis*-3-penten-1-yl nitrite, *trans*-3-penten-1-yl nitrite, and 2-methyl-3-buten-1-yl nitrite, respectively, could be discerned. This indicates that either the photoelectron spectra of the cis and trans radicals are very similar or that the radical isomers interconvert even at a low pyrolysis temperature under our experimental conditions. The 1-methylallyl radical photoelectron spectrum, obtained by pyrolysis of 2-methyl-3-buten-1-yl nitrite, was also studied as a function of temperature but did not appear to change over the 630–765 °C range using the short pyrolyzer.

The small peak at 9.0 eV in Figure 3 is due to He Iβ ionization of CH_2O and a small amount of 1,3-butadiene and/or 2-butene. A smooth band begins at ~8.7 eV. Since the band is without a characteristic peak, any assignment can only be tentative. The ratio of this band to the radical band does not appear to change with the extent of nitrite decomposition. Although this would not be expected for a band due to radical recombination products, it should be noted that this band is in the correct spectral region to arise from these products. The first two photoelectron bands of a C_8, nonconjugated diene with double bonds at the end of the hydrocarbon chains would be expected to overlap each other and result in a fairly smooth band in the 9.0–10.5 eV spectral region.[25,26] Two of the three possible recombination products of 1-methylallyl radical have inner double bonds, which should cause the spectrum to be shifted by a few tenths of an electron volt. For example, the adiabatic IP of 2-butene is 0.5 eV lower than that of 1-butene.[23] Similar smooth bands in the allyl[15] and 2-methylallyl radical spectra, located in the 9–10 eV spectral region, could also be due to dienes produced by radical recombination.

Photoionization of a radical in its doublet state can produce both singlet and triplet spin states of the ion. No calculations of the excited triplet state of 1-methylallyl cation have been done. However, the energy gap between the ground and first excited triplet state of 1-methylallyl cation would not be expected to differ greatly from that for allyl cation. The first excited triplet state of allyl cation has been calculated to be 3.01[27] and 3.67 eV[28] above the ground state. Therefore, it is unlikely that the first excited triplet state of the 1-methylallyl cation gives rise to the band observed at ~9 eV. A discrete band in the 10–11 eV spectral region could not be identified.

2-Methylallyl Radical. The photoelectron spectrum of the pyrolysis products of the 2-methylallyl radical precursor, using the short pyrolyzer at 739 °C, is shown in Figure 4. Count rates at the radical band maximum were ~115 s^{-1}. Vibrational fine structure is clearly resolved. The first two peaks of the vibrational progression, at 7.90 ± 0.02 and 7.95 ± 0.02 eV, correspond to the adiabatic and vertical IPs, respectively. A third peak is also resolved. The spacing between the peaks is more highly reproducible than their positions and was determined to be 0.051 ± 0.003 3V (410 ± 30 cm^{-1}). A previous electron-impact determination yielded an IP of 7.89 eV,[4] in excellent agreement with our adiabatic IP.

The band with an onset ~8.8 eV may be due to the 2-methylallyl radical recombination product, as discussed above. No discrete band ~3 eV above the first photoelectron band of 2-methylallyl radical, which might be assigned to the first excited triplet state of the cation, could be identified.

Allylcarbinyl Radical. An isolated spectrum of the allylcarbinyl radical could not be obtained. At temperatures necessary for nitrite pyrolysis, allylcarbinyl radical itself isomerized or decomposed to products, the spectra of which overlapped its own. Figure 5 is a Ne I spectrum of the pyrolysis products of the allylcarbinyl radical precursor taken with use of the short pyrolyzer at the lowest temperature (583 °C) where significant amounts of the allylcarbinyl radical are produced. Two separate radical bands can be clearly identified in the 7.4–8.8 eV spectral region. The relative intensity of the two bands is temperature dependent, indicating the bands arise from different species. At lower temperatures, the allylcarbinyl radical band is more intense. The vertical IP is determined to be 8.47 ± 0.05 eV. A large uncertainty is assigned to this value since the band top is fairly flat. The vertical IP of allylcarbinyl radical could possibly be even lower than the minimum value included in the error limits if the rising background seen at higher IPs (due to unidentified pyrolysis products) extends significantly into the region of the radical bands. Count rates at the allylcarbinyl radical band maximum were ~22 s^{-1}. The adiabatic IP was chosen as the apparent band onset, at 8.04 eV. However, since the radical band at lower IP may conceal the true onset of the allylcarbinyl radical band, we assign error limits of +0.03 and −0.1 eV to the adiabatic IP. No previous measurements have been made of the IP of this radical.

The band at lower ionization energies is assigned to 1-methylallyl radical. 1,3-Butadiene is also observed, and it increases with pyrolysis temperature. The peaks at 9.7 and 9.9 eV, which are small in the low-temperature spectrum, increase with temperature. A small peak at 10.3 eV is only observed at low temperatures. These features are not due to any expected decomposition product of C_4H_7 radicals, and perhaps they indicate alternative decomposition pathways for the nitrite precursor.

Cyclobutyl Radical. Shown in Figure 6 is a spectrum taken with He I radiation of the pyrolysis products of the cyclobutyl radical precursor produced with use of a low pyrolysis temperature (595 °C) for the short pyrolyzer. Count rates at the cyclobutyl radical band maximum were ~45 s^{-1}. Vibrational fine structure appears on the cyclobutyl radical band. The first two peaks of the vibrational progression, at 7.54 ± 0.02 and 7.66 ± 0.02 eV, correspond to the adiabatic and vertical IPs, respectively. A third peak in the progression is also resolved. The spacing between the peaks is somewhat more highly reproducible than their positions and was determined to be 0.123 ± 0.01 eV (990 ± 100 cm^{-1}). A previous electron-impact determination yielded an IP of 7.88 ± 0.05 eV,[5a] which is much higher than the values reported here. However, the identity of the radical was somewhat uncertain.[5b]

The cyclobutyl radical spectrum could only be obtained at the lowest temperature where significant nitrite decomposition occurred. At higher temperatures, as shown in Figure 7, the radical band in the 7.3–7.8 eV spectral region is much less sharply structured. This is taken to indicate that the first photoelectron band of 1-methylallyl radical, a product of ring opening of cyclobutyl radical itself, is the dominant component of this band. Previously described experiments provide confirmation that the radical spectrum obtained from the cyclobutyl radical precursor is indeed due to cyclobutyl radical and not to 1-methylallyl radicals of a very different isomeric composition than seen at higher pyrolysis temperatures. Under the same conditions at which the cyclobutyl radical band is observed, pyrolysis of the precursors which specifically form either *cis*- or *trans*-1-methylallyl radical as their initial product results in the same rounded, weakly structured 1-methylallyl radical band. 1,3-Butadiene, present at low temperatures, increases with temperature.

As discussed in the section on radical thermal decomposition and isomerization, the direct product of cyclobutyl radical ring opening is presumably the allylcarbinyl radical, but since it is born with ~35 kcal/mol of internal energy it quickly isomerizes to 1-methylallyl radical and/or decomposes to 1,3-butadiene. This is supported by the observation of bands which can be assigned to 1-methylallyl radical and 1,3-butadiene in the pyrolysis spectrum of the nitrite precursor to allylcarbinyl radical.

Pyrolysis of the Cyclopropylcarbinyl Radical Precursor. A He I spectrum of the pyrolysis products of the cyclopropylcarbinyl radical precursor at a moderate pyrolysis temperature (550 °C) for the long pyrolyzer is shown in Figure 8. At room temperature the rate of ring opening of cyclopropylcarbinyl radical to form allylcarbinyl radical in solution is 1.3×10^8 s^{-1}.[29] Thus, we would not expect to observe the photoelectron spectrum of cyclopropylcarbinyl radical. However, the observation of the pyrolysis products of cyclopropylcarbinyl radical further supports our assignments of the other C_4H_7 radical photoelectron spectra. The first photoelectron bands of the ring-opened product of cyclo-

---

(25) Schweig, A.; Weidner, U.; Berger, J. G.; Grahn, W. *Tetrahedron Lett.* **1973**, 557.

(26) Bunzli, J. C.; Burak, A. J.; Frost, D. C. *Tetrahedron* **1973**, *29*, 3735.

(27) Levin, G.; Goddard, W. A., III; Huestis, D. L. *Chem. Phys.* **1974**, *4*, 409.

(28) Peyerimhoff, S. D.;Buenker, R. J. *J. Chem. Phys.* **1969**, *51*, 2528.

(29) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024.

Table II. Thermochemical Data for 1-Methylallyl, 2-Methylallyl, Allylcarbinyl, and Cyclobutyl Systems[a]

R	ΔH_f (R)[b]	ΔH_f (R^+)[c,d]	*D*-(R–H)[c,e]	*D*-(R^+–H^-)[c,e]	PA-(olefin)[e]
1-methylallyl	30.4	203.1	82.7[g]	238.0[g]	188.7
2-methylallyl	30.0	212.2	86.4	251.2	
allylcarbinyl	45.6[f]	231.0	97.9[f]	265.9	160.8
cyclobutyl	51.2	225.1	96.5	253.0	178.1

[a] All values in kcal/mol at 298 K. [b] Taken from ref 11, except for allylcarbinyl radical. [c] Ionic heats of formation are calculated by using the convention that the heat of formation of an electron at rest is zero at all temperatures. Accordingly, $\Delta H_f(H^+)$ = 365.7 kcal/mol and $\Delta H_f(H^-)$ = 34.7 kcal/mol (ref 37). [d] Error limits: ±1.4 kcal/mol for 1-methylallyl; ±1.6 kcal/mol for 2-methylallyl; ±3 kcal/mol for allylcarbinyl; ±1.1 kcal/mol for cyclobutyl. [e] Alkane and olefin heats of formation from ref 38. [f] ΔH_f(allylcarbinyl) calculated assuming *D*(R–H) = *D*(*n*-propyl-H) taken from ref 11. [g] Olefin is 1-butene. *D*(R–H) = 85.5 kcal/mol and *D*(R^+–H^-) = 240.8 kcal/mol if *trans*-2-butene is the olefin.

propylcarbinyl radical, allylcarbinyl radical, and the isomerization product of allylcarbinyl radical, 1-methylallyl radical, are observed. The relative intensity of the bands is temperature dependent, the allylcarbinyl radical spectrum being more intense at lower temperatures. 1,3-Butadiene is also observed.

No unassigned alkyl radical band was observed in the pyrolysis spectra of the cyclopropylcarbinyl radical precursor, although a weak band due to cyclopropylcarbinyl radical in the 7.5–9.0 eV spectral region would be obscured by the photoelectron bands of products of cyclopropylcarbinyl radical rearrangement. It is difficult to estimate the IP of cyclopropylcarbinyl radical. Combining one tentative heat of formation for cyclopropylcarbinyl cation of 212 kcal/mol[30–32] (see Discussion below) with the heat of formation of cyclopropylcarbinyl radical[33] yields an adiabatic IP of ~7.1 eV for cyclopropylcarbinyl radical. This is much lower than that of a typical primary radical. For example, the adiabatic IP of isobutyl radical is 7.93 (+0.03 or −0.1) eV.[34] Therefore, depending on the stability of cyclopropylcarbinyl cation, the adiabatic IP of cyclopropylcarbinyl radical is probably between 7.0 and 8.0 eV.

Discussion

The results of the present experiments can be combined with known thermochemistry for the radicals to yield information about the thermochemistry of the carbonium ions. Photoelectron band shapes and resolved vibrational structures are indicative of the extent and type of geometry changes which the radical undergoes upon ionization. Thermal decomposition and isomerization reactions of C_4H_7 radicals can be identified in the temperature-dependent spectra of the pyrolysis products of the radical precursors.

Thermochemistry. Table II summarizes the thermochemistry for the 1-methylallyl, 2-methylallyl, allylcarbinyl, and cyclobutyl systems. From known radical heats of formation and the adiabatic IPs determined from the photoelectron spectra, the heats of formation of the corresponding ions in their ground electronic states with structures similar to those of the radicals can be determined. The values assigned to the cation heats of formation are necessarily subject to change with the values used for the radical heats of formation.[35] The relative energetics of the radicals and ions are shown in Figure 9. Not all of these ionic species may be at local minima on the $C_4H_7^+$ potential energy surface. In particular, allylcarbinyl cation may not be at a local minimum.[6,13b] Although experimental evidence seems to indicate that cyclobutyl cation is a stable gas-phase species,[6–8] theory has not found a local minimum corresponding to this structure.[13a,c] If the cation with the radical-like structure is not at a local minimum, then the apparent adiabatic IP reported here for the radical is not a true adiabatic IP since the ion is not formed in a ground vibrational state. However, because Franck–Condon factors govern the photoionization process, the apparent adiabatic IP still is a very useful thermochemical quantity. It corresponds to

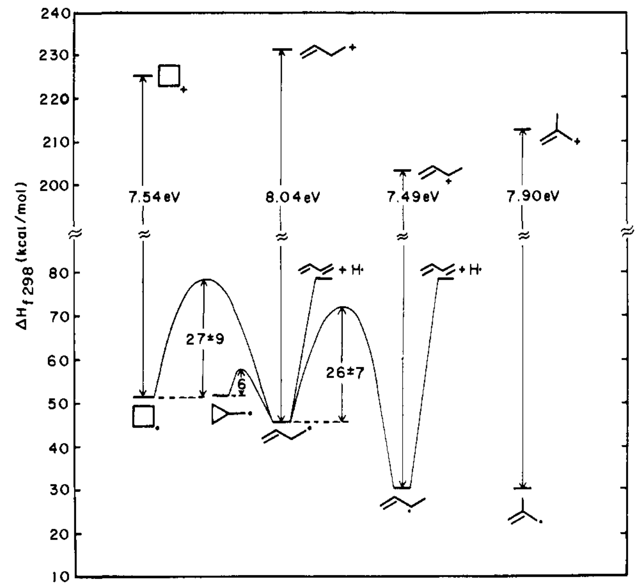


Figure 9. Heats of formation of C_4H_7 radicals and ions and C_4H_7 radical rearrangement energetics.

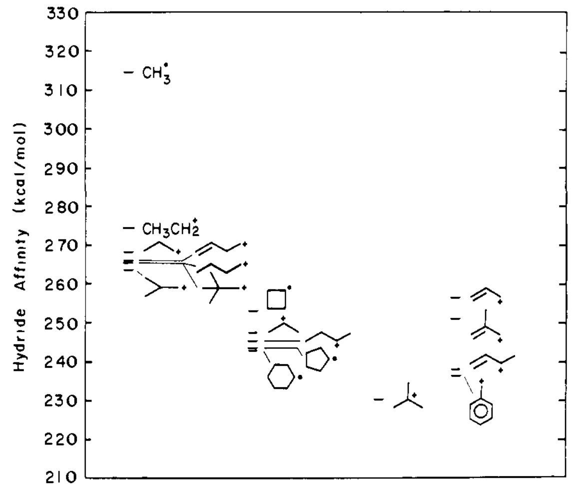


Figure 10. Hydride affinities of the $C_4H_7^+$ ions determined in this work are compared with those of other ions also derived from the photoelectron data of the corresponding radical.[41]

---

(30) Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. II, Chapter 9. Proton affinities in this reference are relative to the proton affinities of isobutene and ammonia at 196.9 and 205.0 kcal/mol, respectively.

(31) The cation heat of formation has been calculated from the proton affinity of the olefin (ref 30) by using the conventions in Table II.

(32) Aue, D. H., private communication. The result and tentative interpretation are published in ref 30 without experimental details.

(33) McMillen, D. F.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1971**, *3*, 359.

(34) Schultz, J. C.; Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.*, accepted for publication.

(35) Recently, the accuracy of the widely accepted Benson values for the heats of formation of alkyl radicals, other than methyl, has been questioned (ref 36). Many experiments by other workers, involving mainly ethyl, isopropyl, and *tert*-butyl radicals, have suggested that alkyl radical heats of formation should be revised slightly upward. The values for the radical heats of formation used in this work have been taken from ref 11, which contains a somewhat updated version of the previously well-accepted Benson values and offers the most self-consistent set available for the radicals studied here. The values assigned to the cation heats of formation will change slightly according to the set of radical heats of formation used. However, the conclusions in this work will remain largely unchanged since most of them are based on relative heats of formation of allyl cations or alkyl cations, the values for which are only very weakly dependent on the set of radical heats of formation used.

formation of the most stable cation obtained by small deviations from the radical geometry. By combining the heat of formation for the ion with alkane and alkene heats of formation, the hydride affinity of the ion and the proton affinity of the corresponding alkene can be determined. Since typical primary, secondary, and tertiary ions have characteristic hydride affinities,[39,40] the hydride affinities of the $C_4H_7^+$ ions can be used to evaluate their relative stabilities. In Figure 10, hydride affinities[41] derived from the photoelectron data on the corresponding radicals obtained in our laboratory[15,34,42-44] are shown for comparison with the $C_4H_7^+$ hydride affinities.

The heat of formation of 1-methylallyl cation is 203.1 ± 1.4 kcal/mol. This is consistent with a heat of formation of 199 kcal/mol calculated from the measured proton affinity of 1,3-butadiene.[30,31] The heat of formation of 2-methylallyl cation is 212.2 ± 1.6 kcal/mol. The adiabatic IPs of 1-methylallyl and 2-methylallyl radicals are 0.64 and 0.23 eV lower, respectively, than that of the parent allyl radical.[15] Methyl substitution at the terminal carbon has a small stabilizing effect and at the central carbon has no apparent effect on the allylic radical, as indicated by the homolytic bond energies of the corresponding olefins. The C–H bond energies in the butenes, listed in Table II, to form 1-methylallyl radical are somewhat lower than the C–H bond energy to form 2-methylallyl radical, which is equal to the C–H bond energy (86.3 kcal/mol[11]) in propylene to form allyl radical. The lowering of the allyl radical ionization potential upon methyl substitution indicates that allyl cation is more stabilized by methyl substitution than allyl radical. Since the ionization potential of 1-methylallyl radical is 0.41 eV lower than that of 2-methylallyl radical, methylation at a terminal carbon in allyl cation results in significantly more stabilization than the same substitution at the central carbon.

Greater stabilization of allyl cations by methylation at a terminal compared to a central carbon has been noted previously.[45] This stabilization of allyl cation can be related to that observed in alkyl cations. ^{13}C NMR spectra and π-electron densities calculated by ab initio molecular orbital theory of substituted allyl cations have been interpreted by considering two contributing ionic resonance structures, the ionic center being on either of the two terminal allylic carbons.[45,46] Both resonance structures for 2-methylallyl cation have primary ionic centers, like allyl cation. In this case, the amount of stabilization is what would be expected for methyl substitution at a carbon one removed from a primary alkyl cation center. The hydride affinity of 2-methylallyl cation (251.6 kcal/mol) is 4.8 ± 2 kcal/mol less than that of allyl cation (256.4 kcal/mol[15,41]). This is equal to the 5.0 ± 3 kcal/mol stabilization observed when the hydride affinity of isobutyl cation (263.4 kcal/mol) is compared to that of *n*-propyl cation (268.4 kcal/mol).[34,41] β-Methyl stabilization of primary alkyl cations has been ascribed to both inductive and hyperconjugative effects.[47] In the case of 1-methylallyl cation, one resonance structure has a secondary and the other a primary cationic center. Referring to Figure 10, the hydride affinity of 1-methylallyl cation (238.0 or 240.8 kcal/mol, to form 1- or 2-butene, respectively) is consistent with that which would have been predicted (~244 kcal/mol) for an allylic resonance stabilized average of a primary and secondary C_4 cation.

The heat of formation and hydride affinity of allylcarbinyl cation are 231.0 and 265.9 ± 3 kcal/mol, respectively. The adiabatic IP of allylcarbinyl radical is 8.04 (+0.03 or 0.1) eV. This is comparable to adiabatic IPs of other primary radicals, such as *n*-propyl (8.15 ± 0.02 eV)[34] and *n*-butyl (8.02 (+0.04 or −0.1)).[34] The hydride affinity of allylcarbinyl cation is also comparable to hydride affinities of other primary cations, as seen in Figure 10. Thus, allylcarbinyl cation appears to be a typical primary cation represented by structure IIIa, not stabilized by charge delocalization, as shown in structure IIIb. However, the hydride affinity is not known better than ±3 kcal/mol. If stabilization due to charge delocalization were less than or equal to ~3 kcal/mol, it cannot be detected in these experiments.

The heat of formation of cyclobutyl cation is 225.1 ± 1.1 kcal/mol. The adiabatic IP of cyclobutyl radical (7.54 ± 0.02 eV) is ~0.25 eV higher than would be estimated by considering the IPs of other secondary radicals, such as isopropyl (7.36 ± 0.02 eV),[34] *sec*-butyl (7.25 ± 0.02 eV),[34] cyclopentyl (7.21 ± 0.02 eV),[43,44] and cyclohexyl (7.15 ± 0.04 eV)[43,44] radicals. The C–H bond-dissociation energy of cyclobutane is 1.0 kcal/mol greater than the secondary C–H bond energy in *n*-butane,[11] indicating a small amount of extra energy is needed to form a radical center in cyclobutane compared to other alkanes. The higher adiabatic IP for cyclobutyl radical indicates that even more additional energy is needed to form a cation center in cyclobutane compared to other alkanes. This is reflected in the hydride affinity of cyclobutyl cation, which is ~8 kcal/mol greater than that expected for a secondary C_4 cation (see Figure 10). With use of the hydride affinity as a measure of relative cation stabilities, cyclobutyl cation is ~8 kcal/mol less stable than a typical secondary C_4 cation. This may be a somewhat exaggerated estimate of the instability of the cyclobutyl cation, since for all the other secondary radicals, except for isopropyl radical, the photoelectron band onset was chosen as the adiabatic IP, since no vibrational structure could be resolved on these bands. If the photoelectron band onset for cyclobutyl radical (~7.40 eV) is used to estimate the lowest energy cyclobutyl cation formed by photoionization of the radical, then the cyclobutyl cation is ~5 kcal/mol less stable than a typical secondary cation. As will be discussed later in the section on ionic structures, this instability of the cyclobutyl cation is probably a result of its somewhat rigid four-membered ring structure. The peak assigned to the adiabatic IP may also not arise from the 0–0 transition. If Franck–Condon factors are not favorable enough to observe the 0–0 transition, the reported heat of formation of the ion is then an upper limit.

From the photoelectron data, the proton affinity of cyclobutene to form cyclobutyl cation is calculated to be 178.2 kcal/mol. An experimental determination of the proton affinity of cyclobutene yielded a value of 191 kcal/mol.[30] An ICR bracketing technique was used, where it was observed whether a proton transfer reaction with cyclobutene was exothermic or endothermic. No equilibria was established.[32] If a $C_4H_7^+$ cation is being formed at its threshold through the proton-transfer reaction, then it has a heat of formation of 212 kcal/mol.[31] It cannot correspond to a $C_4H_7^+$ cation with the cyclobutyl cation structure accessed by photoionization of the cyclobutyl radical, which has a heat of formation 11 kcal/mol higher. It is interesting to note that a cyclopropylcarbinyl structure for the cation has been suggested[30,32] and was recently supported by a good agreement between STO-3G ab initio calculations[48] of heats of isodesmic reactions involving cyclopropylcarbinyl cation and the experimental values calculated by using 212 kcal/mol for the heat of formation of the cation.

Cation Structures. The shape of the first photoelectron band, being determined by Franck–Condon factors between the radical

---

(36) For critical reviews, see ref 11 and: Purnell, J. H. In "Frontiers in Free Radical Chemistry"; Pryor, W. A., Ed.; Academic Press: New York, 1980; p 93. For references to the most recent work, see: Doering, W. v. E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279.

(37) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl. 1.* **1977**, *6*.

(38) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

(39) Lossing, F. P.; Maccoll, A. *Can. J. Chem.* **1976**, *54*, 990.

(40) Goren, A.; Munson, G. *J. Phys. Chem.* **1976**, *80*, 2848.

(41) Hydride affinities were calculated by using the conventions in Table II, radical heats of formation (ref 11, or estimated from bond energies in this reference), adiabatic IPs for the radical (ref 15, 34, 42–44), and alkane or alkene heats of formation (ref 38). Note that the values assigned to the hydride affinities are necessarily subject to change with the values used for the radical heats of formation (ref 34 and 35).

(42) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067.

(43) Houle, F. A.; Beauchamp, J. L. *J. Phys. Chem.* **1981**, *85*, 3456.

(44) Houle, F. A.; Beauchamp, J. L.; Prakash, G. K. S.; Olah, G. A., unpublished results.

(45) Mayr, H.; Forner, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 6032.

(46) Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 1539.

(47) Radom, L.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 5935.

(48) Schmitz, L. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1982**, *104*, 2605.

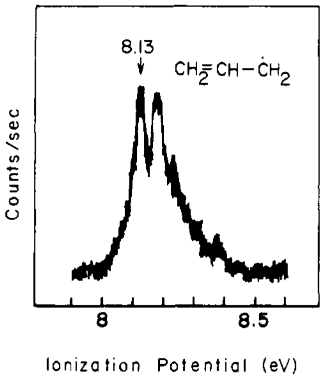


Figure 11. He I spectrum of allyl radical. Data were taken from ref 15.

and the cation in their ground electronic states, provides information regarding the relative shapes of the ionic and radical potential energy surfaces in the region of the radical geometry. If adiabatic and vertical IPs coincide, the equilibrium nuclear coordinates of the radical and cation differ little. Vibrational fine structure on the photoelectron band then indicates changes in force constants upon ionization. If the adiabatic and vertical IPs do not coincide, the difference between them indicates the extent to which the equilibrium geometry of the cation differs from that of the radical.

1-Methylallyl radical and 2-methylallyl radical have quite differently shaped first photoelectron bands, although they are both methyl-substituted allyl radicals. 1-Methylallyl radical and cation can take on both trans and cis conformations (Va and Vb, respectively). The photoelectron spectrum of 1-methylallyl radical is due to ionization of radicals with these two different conformations. The presence and specific location of the methyl substituent on the allylic framework also influences the structural changes which occur upon ionization of the unpaired electron in the radical.

2-Methylallyl radical and both cis and trans conformations of 1-methylallyl radical have been observed in ESR experiments[49,50] and identified as π-conjugated radicals. Allyl,[15] benzyl,[15] and cycloheptatrienyl radicals,[9c] all π-conjugated radicals, have first photoelectron bands characterized by sharply resolved vibrational structure with the adiabatic and vertical ionization potentials coinciding. The first photoelectron band of 2-methylallyl radical is very similar to these, especially to that of allyl radical shown in Figure 11. However, the adiabatic IP of 2-methylallyl radical is displaced by 0.05 eV from the vertical IP, indicating that the equilibrium geometry of the cation is slightly different from that of the radical. The most obvious difference between 2-methylallyl and these other π-conjugated radicals is the methyl group, which is attached to the conjugated carbon framework. The near coincidence of the frequencies associated with the vibrational structure resolved on the allyl[15] and 2-methylallyl radical photoelectron bands, 420 and 410 cm^{-1}, respectively, indicates that movement of the methyl group itself is not involved. However, the presence of the methyl group could influence the equilibrium nuclear conformation in the cation associated with this vibrational mode. No assignment of these vibrational frequencies of the ions has been made due to lack of experimental or calculated vibrational frequencies of allyl or 2-methylallyl cation.

The first photoelectron band of 1-methylallyl radical is broader and has less sharply resolved vibrational structure than the other π-conjugated radicals. 1-Methylallyl radical differs from these other radicals due to the unconstrained methyl substituent which allows it to take either a cis or trans conformation. Since pyrolysis takes place under low-pressure, fast-flow conditions, it is difficult to estimate whether an equilibrium is established between *cis*- and *trans*-1-methylallyl radicals because the effective vibrational temperatures of the radicals are unknown. The radicals are probably characterized by temperatures 200–300 °C lower than the furnace temperature.[43] Experimental determinations of $\Delta G^{\ddagger}$ for the trans to cis isomerization of 1-methylallyl radical have yielded values of $\leq$14.4 ± 2[51] and 21 ± 3 kcal/mol,[52] corresponding to rate constants of trans to cis isomerization at an effective temperature of ~300 °C of 4×10^7 and 1×10^5 s^{-1}, respectively. Thus, it is not surprising that the same 1-methylallyl radical spectrum is obtained from precursors which initially produce only *cis*- or *trans*-1-methylallyl radicals. Experimentally, the entropy of *trans*-1-methylallyl radical is $1.4 \pm 2.0 \times 10^{-4}$ kcal/(mol K) greater than that of cis, and the enthalpy of *cis*-1-methylallyl radical is 0.151 ± 0.060 kcal/mol greater than that of trans.[53] When these values are used, and assuming an equilibrium at ~300 °C is reached, the ratio of *trans*- to *cis*-1-methylallyl radical is ~1.2:1.0.

Ab initio calculations on both *trans*- and *cis*-1-methylallyl cation indicate that the trans configuration is lower in energy than the cis by 3.0 kcal/mol at the STO-3G level[45] and 3.36 kcal/mol at the 4-31G level.[54] The radical also prefers to be trans, but only by 0.2 kcal/mol from experimental evidence[53] and by 1.02 kcal/mol from a 4-31G calculation.[54] From these energy differences, the adiabatic IP of *trans*-1-methylallyl radical is estimated to be ~0.09–0.14 eV lower than that of *cis*-1-methylallyl radical. On the basis of these studies, the adiabatic IP determined in this work is assigned to the trans isomer.

The much more subtle orientational preference of the methyl rotor about the allylic framework of 1-methylallyl radical and cation has also been noted in theoretical studies. As determined by STO-3G ab initio calculations,[54] the preference for a specific rotational conformation of the methyl group changes by <1 kcal/mol going from the radical to the cation for both cis and trans isomers. These changes are not great enough to displace the vertical from the adiabatic IP. However, they may cause excitation of low-frequency torsional modes upon ionization, which will tend to wash out or broaden structure that would otherwise be much more sharply resolved.

On ionization of isopropyl and *tert*-butyl radicals, systems where methyl groups are bound to a radical center, C–C stretching modes are excited.[42] Theoretical calculations[54] on 1-methylallyl radical and cation did not optimize the $C{-}CH_3$ bond distance and thus did not examine the changes in this bond distance which may occur on ionization of the radical. However, by comparison with the isopropyl and *tert*-butyl systems, excitation of the $C{-}CH_3$ stretching mode would be expected on ionization of 1-methylallyl radical. This difference in equilibrium geometry between radical and cation could result in the vertical IP being displaced from the adiabatic IP.

Thus, there are several factors which may contribute to producing a first photoelectron band for 1-methylallyl radical which is quite different from those of allyl or 2-methylallyl radical. Both cis and trans spectra may look different from that of the other two allyl radicals due to excitation upon ionization of a low-frequency torsional mode and a C–C stretching mode. Overlapping of the cis and trans photoelectron bands may serve to mask some of the structure present on the individual bands, and most likely prevented us from identifying vibrational progressions on the structured band.

ESR data on allylcarbinyl radical in solution are typical of those expected for a primary radical,[56] showing no evidence for significant homoconjugation between the unpaired electron and the π electrons in the double bond.[55,57,58] Theory is in agreement.[59]

---

(49) Kochi, J. K.; Krusic, P. J. *J. Am. Chem. Soc.* **1968**, *90*, 7157.

(50) Linder, R. E.; Winters, D. L.; Ling, A. C. *Can. J. Chem.* **1976**, *54*, 1405.

(51) Gorton, P. J.; Walsh, R. *J. Chem. Soc., Chem. Commun.* **1972**, 783.

(52) Crawford, R. J.; Hamelin, J.; Strehlke, B. *J. Am. Chem. Soc.* **1971**, *93*, 3810.

(53) Montagne, D. C. *Int. J. Chem. Kinet.* **1973**, *5*, 513.

(54) Schleyer, P. v. R.; Dill, J. D.; Pople, J. A.; Hehre, W. J. *Tetrahedron* **1977**, *33*, 2497.

(55) Proton and carbon positions are defined by using the convention that the radical center is at C_α and the α protons are bound to C_α; ref 56.

(56) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

(57) Chen, K. S.; Edge, D. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7036.

(58) Fessenden, R. W. *J. Chim. Phys. Phys.-Chim. Biol.* **1964**, *61*, 1570.

Table III. Comparison of the First Photoelectron Bands of Cyclic and Acyclic Secondary Radicals[a]

R	band onset	vertical IP	vertical IP - onset
c-C_4H_7	~7.40	7.66	~0.26
c-C_5H_9	7.21	7.46	0.25
c-C_6H_{11}	7.15	7.40	0.25
i-C_3H_7	7.36	7.69	0.33
sec-C_4H_9	7.25	7.59	0.34

[a] All quantities in eV. Cyclobutyl data from this work. Cyclopentyl and cyclohexyl data from ref 43 and 44. Isopropyl and *sec*-butyl data are taken from ref 15 and 34, respectively.

These results justify our use of a primary C–H bond energy to estimate the heat of formation of allylcarbinyl radical. We would expect that a typical primary ion (IIIa) would be formed on ionization of the radical, not a geometrically constrained, delocalized allylcarbinyl cation (IIIb). The thermochemistry of the allylcarbinyl system supports this.

The first photoelectron band of allylcarbinyl radical is broad and featureless, as is the first photoelectron band of *n*-butyl radical.[34] *n*-Propyl radical has a broad photoelectron band, although weak fine structure is resolved on the low ionization potential side of the band.[34] A featureless band for allylcarbinyl radical is not unreasonable, due to excitation of several vibrational and torsional modes on ionization. Absence of a local minimum on the $C_4H_7^+$ potential surface for allylcarbinyl cation could also result in a smooth photoelectron band. If photoionization forms an ion on a descending part of a very broad potential energy surface, vibrational states may be so closely spaced as to result in a smoothly varying photoelectron band.

ESR data have been interpreted to indicate that in solution cyclobutyl radical has a planar,[56,60] or "essentially" planar,[61] radical center since its α-proton hyperfine splitting is similar to a value characteristic of a π-electron radical center and to those of other secondary radicals. A small degree of nonplanarity in its equilibrium conformation cannot be ruled out since there is a question as to whether acyclic alkyl radicals are planar or slightly nonplanar.[42] In addition, the ESR data suggest that the ring is planar as well[56,60] or rapidly oscillates between two structures that are very nearly planar.[60]

Semiempirical calculations of cyclobutyl cation have disagreed as to whether the planar or puckered system is more stable.[62–65] In cases where the puckered ring is more stable, substantial 1,3 carbon/carbon cross-ring bonding interactions are shown to contribute special stability to the system.[63,64] Ab initio molecular orbital calculations predict that puckered cyclobutyl cation is not at a minimum on the ionic potential surface.[13] Several experimental results described in the introduction, in particular the kinetic energy release measurements of dissociating $(C_4H_7Br)^+$ ions,[6] indicate that cyclobutyl cation does exist in a potential well in the gas phase.

The general shapes and breadths of the cyclobutyl, cyclopentyl, and cyclohexyl radical[43,44] photoelectron spectra are similar. Since adiabatic and vertical IPs do not coincide, the equilibrium geometry of each ion differs from that of the corresponding radical. From Table III we see that the vertical IPs are displaced only ~0.25 eV from the photoelectron band onsets in these cyclic systems where both radical and ion are fairly constrained as compared to ~0.33 eV for the secondary acyclic systems. Whereas cyclopentyl and cyclohexyl radical bands are featureless, structure due to vibrational excitation is clearly resolved on the cyclobutyl radical band. Explanations given[44] for the absence of structure on the cyclopentyl and cyclohexyl radical photoelectron bands also apply to a comparison between these two cyclic radicals and cyclobutyl radical. Lack of structure may be due to the overlapping of bands arising from ionization of low-lying nondegenerate conformations of the cyclopentyl or cyclohexyl radicals. These radical conformations have been identified in ESR experiments, but ESR experiments on cyclobutyl radical indicate the radical is only in one conformation or possibly rapidly interconverting between degenerate conformations. Excitation of very low frequency vibrations on ionization may also tend to mask structure that would otherwise be observable. The larger, less rigid systems such as cyclopentyl and cyclohexyl radicals, as compared to cyclobutyl radical, would be most likely to manifest this. Finally, absence of structure may be an indication that the ion is not stable with respect to isomerization, resulting in excitation of very closely spaced vibrational states. Therefore, the presence of structure on the cyclobutyl radical band is consistent with cyclobutyl cation being at a local minimum on the $C_4H_7^+$ potential energy surface, as indicated by experiments.[6–8]

The resolved vibrational progression on the cyclobutyl radical photoelectron spectrum, characterized by a frequency of 990 ± 100 cm^{-1}, has not been assigned. Those vibrations corresponding most closely to the change in equilibrium geometry caused by ionization will be most strongly excited. Since the ring of the radical is planar or nearly so, according to ESR data, and the majority of theoretical calculations assign special stability to cross-ring interactions in cyclobutyl cation, a ring-puckering mode may be excited. However, it probably would not be resolved in the photoelectron spectrum of cyclobutyl radical since the ring-puckering mode in cyclobutane has a frequency of 200 cm^{-1}.[66] Ring-deformation modes may also be excited. In cyclobutane, ring-deformation modes involve C–C stretching, C–C–C bending, and CH_2 deformation and have frequencies of ~1000 cm^{-1}. An assignment is also suggested by consideration of the photoelectron spectrum of another secondary radical, that of isopropyl radical.[42] A resolved progression of 970 cm^{-1} on the first photoelectron band of isopropyl radical was assigned to a mixed, totally symmetric C–C stretching, HCC bending (at the CH_3 groups) mode of the ion. If the geometry changes occurring upon ionization of cyclobutyl radical are similar to those occurring at the isopropyl radical center, then the 990-cm^{-1} vibrational progression may arise from excitation of an analogous skeletal deformation mode of cyclobutyl cation, which would be similar to the ring-deformation modes in cyclobutane.

As mentioned in the section on ion thermochemistry, the adiabatic IP of cyclobutyl radical corresponds to formation of an ion that is less stable, by 5 to 8 kcal/mol, than would be predicted for a C_4 secondary cation, based on the hydride affinities of acyclic and cyclopentyl and cyclohexyl cations. The difference between the band onset and vertical IP for cyclobutyl radical is nearly the same as for cyclopentyl and cyclohexyl radicals (see Table III). Thus, cyclobutyl cation achieves the same amount of stabilization, by small deviations from the equilibrium radical geometry, as do cyclopentyl and cyclohexyl cations, which appear to be normal secondary cations as indicated by their hydride affinities.

One possible explanation for the higher adiabatic (and vertical) IP for cyclobutyl radical than would be expected for a typical C_4 secondary radical derives from a consideration of the effect of the strained four-membered ring system on the radical center. Slower rates of hydrogen abstraction from cyclobutane and the stronger C–H bond in cyclobutane compared to cyclopentane and cyclohexane, have been explained by a small increase in the s character of the C–H bonds in cyclobutane.[64] The carbon hybrid orbitals which form the ring C–C bonds have more p character than pure sp^3 hybrids, to minimize strain in the ring, and thus the carbon orbitals participating in the C–H bonds have more s character. If the unpaired electron in cyclobutyl radical also occupies an orbital with more s character than other secondary radicals, it is more strongly bound and thus the energy to ionize it is greater.

---

(59) Hehre, W. J. *J. Am. Chem. Soc.* **1973**, *95*, 2643.

(60) Zhidomirov, G. M.; Abronin, I. A.; Micheikin, I. D.; Chuvylkin, N. D. *J. Magn. Reson.* **1975**, *17*, 161.

(61) Kochi, J. K. *Adv. Free-Radical Chem.* **1975**, *5*, 189.

(62) Davis, R. E.; Ohno, A. *Tetrahedron* **1968**, *24*, 2063.

(63) Baldwin, J. E.; Foglesong, W. D. *J. Am. Chem. Soc.* **1968**, *90*, 4311.

(64) Bauld, N. L.; Cessac, J.; Holloway, R. L. *J. Am. Chem. Soc.* **1977**, *99*, 8140.

(65) Wiberg, K. B.; Szeimies, G. *J. Am. Chem. Soc.* **1970**, *92*, 571.

(66) "Tables of Molecular Vibrational Frequencies;" National Bureau of Standards: Washington, DC, 1968; Part II.

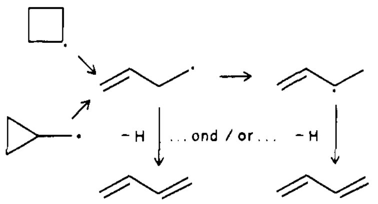


Figure 12. Major thermal decomposition and isomerization pathways for C_4H_7 radicals as observed by photoelectron spectroscopy.

If this explanation is correct, the ESR α-proton coupling constant is not sensitive to the (probably small) increased nonplanarity at the cyclobutyl radical center compared to other secondary radical centers. The cation formed by photoionization of the radical is less stable than a typical secondary ion because the planar configuration preferred by a cation center is opposed by the nonplanar center preferred by the four-membered ring. The puckered cyclobutyl cation, with its extremely nonplanar cation center, may be a more stable conformation of the cyclobutyl cation. However, Franck–Condon factors for transition to this structure of the cation from the radical would be very small.

Radical Thermal Decomposition and Isomerization. By photoelectron spectroscopy, both reactive intermediates and stable species may be directly observed, so that products of radical pyrolysis may be identified.[43,44] Overlapping photoelectron spectra may obscure some products so that in general only the major products can be identified clearly. Those species with lifetimes ~1 ms can be observed.

A simple scheme, presented in Figure 12, can account for all the products identified in the pyrolysis spectra of 1-methylallyl, allylcarbinyl, cyclobutyl, and cyclopropylcarbinyl radicals. 2-Methylallyl radical neither isomerizes to any other C_4H_7 radical nor is it a product of their isomerization reactions. The radical recombination products tentatively identified in the 1- and 2-methylallyl radical pyrolysis spectra are not included in this scheme. A diagram of the energetics for the unimolecular radical rearrangements and decomposition reactions is included in Figure 9. As noted in the Experimental Section, some of these reactions may in fact take place on the pyrolyzer wall.

Both 1- and 2-methylallyl radical are very stable. No major radical decomposition or isomerization products are seen in the pyrolysis spectra of 2-methylallyl radical, and only a small amount of 1,3-butadiene and/or 2-butene is observed at high temperatures in the pyrolysis spectra of 1-methylallyl radical.

At the lowest temperature at which the nitrite precursor of allylcarbinyl radical decomposes to form this initial radical, both 1-methylallyl radical and 1,3-butadiene are formed. The isomerization of allylcarbinyl radical to 1-methylallyl radical has been proposed to account for the products of radical scavenging in chemically and thermally activated radical decompositions.[68-70] An activation energy of 20.0 ± 0.7 kcal/mol was determined for the thermal radical isomerization.[68,70] The best agreement between rate constants calculated by RRKM theory applied to a 1,2-H shift mechanism and experimental rate constants obtained in chemical-activation studies was found when the threshold energy is 33.0 kcal/mol and log A (s^{-1}) is 12.68.[69] Other mechanisms, such as a 1,3-H shift, were not considered. 1,3-Butadiene is the other thermolysis product of allylcarbinyl radical. Production of 1,3-butadiene in the high-pressure experiments, where radical scavenging techniques are used, is accounted for by disproportionation reactions involving allylcarbinyl or 1-methylallyl radical.[69,71,72] The other products of disproportionation reactions, 1-butene and 2-butene, are not observed in the photoelectron spectra. A small amount of what may be 1,3-butadiene is observed in the pyrolysis spectra of 1-methylallyl radical. Therefore, 1,3-butadiene is formed mainly by unimolecular or heterogeneous hydrogen atom loss from allylcarbinyl radical and/or internally excited 1-methylallyl radical, formed by the isomerization of allylcarbinyl radical. A small peak (~13.6 eV) which can be assigned to hydrogen atoms is observed in the high-temperature pyrolysis spectra of the allylcarbinyl radical precursor.

Evidence for both the isomerization of allylcarbinyl to 1-methylallyl radical and the decomposition of allylcarbinyl and/or internally excited 1-methylallyl radical to 1,3-butadiene is also seen in the pyrolysis spectra of the cyclobutyl and cyclopropylcarbinyl radical precursors. Ring opening of cyclobutyl radical to allylcarbinyl radical has been studied by chemical and thermal activation of cyclobutyl radical. With the exception of one determination of 18.1 kcal/mol,[68] values for the activation energy for ring opening of cyclobutyl radical fall in the range of 27–35 kcal/mol.[71,73,74] It is possible to observe the cyclobutyl radical in photoelectron spectra under nearly the same pyrolysis conditions as those required for cyclopentyl and cyclohexyl radicals,[43] whose activation energies for ring opening are 31 and 31–37 kcal/mol, respectively.[71] It is not likely, then, that the activation energy for ring opening of cyclobutyl radical is very different from these values.

The ring-opened product, allylcarbinyl radical, is not observed in the pyrolysis spectra of the cyclobutyl radical precursor. Allylcarbinyl radical presumably isomerizes or decomposes rapidly, since it is born with ~33 kcal/mol of internal energy (see Figure 9). 1-Methylallyl radical and 1,3-butadiene are the major products of cyclobutyl radical thermolysis via the allylcarbinyl radical intermediate.

Ring opening of cyclopropylcarbinyl radical to allylcarbinyl radical has been extensively investigated in recent years.[75] Although this unimolecular reaction is extremely rapid, its rate has been measured in solution by EPR spectroscopy.[29] An activation energy of 5.94 ± 0.57 kcal/mol and a log A (s^{-1}) of 12.43 ± 0.85 were determined. No evidence for cyclopropylcarbinyl radical was observed in photoelectron spectra of the pyrolysis products of the precursor to this radical. This was to be expected for a radical with such a rapid unimolecular decomposition reaction. Instead, the ring-opened product, allylcarbinyl radical, is observed. Combining the heats of formation of cyclopropylcarbinyl radical (51.6 kcal/mol[33]) and allylcarbinyl radical with the activation energy for ring opening of cyclopropylcarbinyl,[29] we can estimate that the allylcarbinyl radical is born with 12 ± 3 kcal/mol internal energy (see Figure 9). This is consistent with the activation energy (9.0 kcal/mol[76]) for the reverse reaction, allylcarbinyl radical ring closing to cyclopropylcarbinyl radical (see below). The isomerization product of allylcarbinyl radical, 1-methylallyl radical, and 1,3-butadiene is also observed in the pyrolysis of the cyclopropylcarbinyl radical precursor.

Allylcarbinyl radical can ring close to cyclopropylcarbinyl radical, but no evidence has been found for formation of cyclobutyl radical from allylcarbinyl radical.[77] The rate of allylcarbinyl ring closure to cyclopropylcarbinyl has been determined by NMR and EPR spectroscopy.[76] These experiments yielded an activation energy of 9.0 ± 0.5 kcal/mol and a log A (s^{-1}) of 10.3 ± 0.5 for this unimolecular reaction. By combining this rate with the rate of cyclopropylcarbinyl radical ring opening,[29] the relative concentration of allylcarbinyl to cyclopropylcarbinyl radical under equilibrium conditions at 300 °C (an average effective pyrolysis temperature) is ~2×10^3. Thus, we would not expect to observe cyclopropylcarbinyl radical in the photoelectron spectra of C_4H_7

---

(67) Tedder, J. M.; Walton, J. C. *Adv. Free-Radical Chem.* **1980**, *6*, 155.

(68) Gordon, A. S.; Smith, S. R.; Drew, C. M. *J. Chem. Phys.* **1962**, *36*, 824.

(69) Ibuki, T.; Tsuji, A.; Takezaki, Y. *J. Phys. Chem.* **1976**, *80*, 8.

(70) Gordon, A. S. *Pure Appl. Chem.* **1962**, *5*, 441.

(71) Stein, S. E.; Rabinovitch, B. S. *J. Phys. Chem.* **1975**, *79*, 191.

(72) Montgomery, L. K.; Matt, J. W.; Webster, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 923.

(73) Walsh, R. *Int. J. Chem. Kinet.* **1970**, *2*, 71.

(74) McMillen, D. F.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1972**, *4*, 487.

(75) Wilt, J. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 8.

(76) Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serelis, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734.

(77) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. I, Essay 4.

radical pyrolysis products due to ring closing of allylcarbinyl radical.

Commentary

The results presented here, in conjunction with the results of other investigations, offer a basis for further studies of the structural identities, corresponding heats of formation, and interconversion pathways of the $C_4H_7^+$ species. Appearance potential measurements for $C_4H_7^+$ fragment ions strongly suggest that an upper limit for the heat of formation of the most stable gas-phase $C_4H_7^+$ ion(s) is 206 ± 2 kcal/mol.[4,10] This coincides, within experimental error, with the heat of formation of 1-methylallyl cation determined in that work (204 ± 3) and in the present study (203.1 ± 1.4 kcal/mol). Other structures may be equally stable. The heats of formation of puckered cyclobutyl cation and bicyclobutonium cation are not known, and only a tentative heat of formation for cyclopropylcarbinyl cation (212 kcal/mol[30,31]) has been proposed. Theoretical studies[13] and NMR experiments under stable-ion conditions[2] indicate that these species are all very close in energy. The slightly puckered cyclobutyl cation is a higher energy species; its heat of formation (225.1 ± 1.1 kcal/mol) was determined in this work. A determination of the ionization potential of cyclopropylcarbinyl radical, providing a definitive value for the heat of formation of cyclopropylcarbinyl cation, would greatly further an understanding of the $C_4H_7^+$ system in the gas phase. Producing the radical by pyrolysis is not the method of choice, as was confirmed in this work. Photolysis of an appropriate precursor would allow more control over the ambient temperature and the distance between radical production and the ionization region.

Recently, the first equilibrium between an allyl and a cyclopropylcarbinyl cation was observed under stable-ion conditions.[78] *cis*-1-Methylcyclopropylcarbinyl cation rearranges at −100 °C to 1-ethylallyl cation. However, interconversion between the parent cyclopropylcarbinyl (or bicyclobutonium) cation and 1-methylallyl cation has not been observed in solution. 1-Methylallyl cation[3] and bicyclobutonium cation[2c] are stable up to −20 and −60 °C, respectively, under stable-ion conditions. Continuation of the experiments to higher temperatures resulted in decomposition reactions of the cations. Significant barriers must exist to prevent the interconversion. For comparison, the rearrangement of *sec*-butyl cation to the more stable *tert*-butyl cation has been observed to take place at a significant rate only above ca. −40 °C.[79] The activation energy for this process, assuming a normal log *A*, was estimated to be ∼18 kcal/mol. In the gas phase, *sec*-butyl cation can also survive without rearrangement to *tert*-butyl cation.[80] Similarly, the significant barrier to interconversion of bicyclobutonium and 1-methylallyl cations observed under stable conditions suggests that separate preparation of the isomers is possible and their rearrangement pathways may be studied in the gas phase or in matrix-isolation experiments where competing side reactions may be avoided.

Acknowledgment. We thank Peter G. Schultz for his help with the preparation of 2-cyclopropylethanol and *cis*- and *trans*-3-penten-1-ol and Dr. José A. Martinho Simões for his help with the preparation of *trans*-3-penten-1-ol. We also thank Professors D. H. Aue, W. J. Hehre, J. D. Roberts, and W. A. Goddard and Dr. A. F. Voter for helpful discussions. This work was supported in part by the Department of Energy and by the President's Fund of the California Institute of Technology.

Registry No. I, 19067-43-7; III, 25268-58-0; V, 17171-50-5; VI, 17542-17-5; 1-methylallyl radical, 15819-46-2; 2-methylallyl radical, 15157-95-6; allylcarbinyl radical, 2154-62-3; cyclobutyl radical, 4548-06-5.

---

(78) Falkenberg-Andersen, C.; Ranganayakulu, K.; Schmitz, L. R.; Sorensen, T. S.,to be published.

(79) Saunders, M.; Hagen, E. L.; Rosenfeld, J. *J. Am. Chem. Soc.* **1968**, *90*, 6882.

(80) Shold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1978**, *100*, 7915.

He I Photoelectron Study of Cyanogen Isothiocyanate, NCNCS, Produced by Thermal Isomerization of Sulfur Dicyanide, $S(CN)_2$

Michael A. King[†] and Harold W. Kroto*

Contribution from the School of Chemistry and Molecular Sciences, University of Sussex, Brighton, UK BN1 9QJ. *Received May 25, 1984*

Abstract: A gas-phase synthesis of cyanogen isothiocyanate, NCNCS, first established by microwave spectroscopy during pyrolysis experiments with sulfur dicyanide, $S(CN)_2$, has been investigated with use of He I photoelectron spectroscopy. The photoelectron spectrum of NCNCS has been analyzed by comparison with the spectra of related molecules and with the aid of MO calculations. The first ionization potential is 10.58 eV. The observed separation of the first two photoelectron bands (associated with ionization from a pair of π orbitals) is shown to be consistent with a CNC bond angle of 155 ± 5°, reflecting the molecule's quasilinear character.

Simple compounds containing the SCN group form an interesting class of molecules for spectroscopic and theoretical studies since the SCN moiety shows ambidentate character, bonding via sulfur to give thiocyanates (RSCN) or via nitrogen to give isothiocyanates (RNCS).[1] For example, the parent acid exists as HNCS,[2] whereas both methyl compounds, CH_3SCN and CH_3NCS, are known.[3] The halogen and pseudohalogen derivatives appear to prefer the thiocyanate form XSCN [X = Cl,[4,5] Br,[5],

---

[†] Present address: Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland.

(1) Guy, R. G. "The Chemistry of Cyanates and Their Thio Derivatives"; Patai, S., Ed.; Wiley: New York, **1977**; Part II, p 819.

(2) Beard, C. I.; Dailey, B. P. *J. Chem. Phys.* **1950**, *18*, 1437.

(3) Lett, R. G.; Flygare, W. H. *J. Chem. Phys.* **1967**, *47*, 4730.

0002-7863/84/1506-7347$01.50/0