is now coupled only to H_b (J_{ab} = 2.4 Hz), both signals appearing as doublets. The previously complex multiplet due to H_c, H_e, and H_f was transformed into an AB quartet ($\Delta\nu_{ef}$ = 5.06 Hz, J_{ef} = 7.2 Hz).

Distinction between the two proposed pathways may be achieved through an analysis of the $C_{22}H_{16}$ dimers produced. A mechanism proceeding via initial allene-allene cycloaddition[21] can lead to but two isomers in which the bicycloheptadiene skeletons remain preserved. The alternate route, involving allene closure followed by addition across the internal bridgehead double bond,[22] may produce four isomers.

Further effort is currently being directed at elucidating the structure of the dimers, as well as surveying the chemistry of **6** and its allene progenitor.

Acknowledgment is made to the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. R.H.L. is grateful to the E. I. duPont de Nemours Company for a Young Faculty Grant and also to Professor W. Doering and two referees for their most helpful comments.

Supplementary Material Available: Fractional coordinates, bond distances, bond angles, and structure factors (12 pages). Ordering information is given on any current masthead page.

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(12) Thanks are due to Dr. M. Saunders (Yale) and Dr. L. Neuringer (Francis Bitter National Magnet Laboratory at M.I.T.) for recording spectra at 270 MHz.

(13) Actually space group $P_{2_12_12_1}$ was the only space group consistent with the systematic extinctions and the lack of molecular symmetry displayed in the NMR spectrum. It would be interesting to know whether this represents a case of spontaneous resolution where each macroscopic crystal contains only one enantiomer or whether the enantiomers occur in resolved microscopic domains scattered throughout the entire crystal. Unfortunately, thk crystal morphology was unsuitable for a visual determination and the lack of anomalous scatterers precluded determination by an x-ray experiment. We were unable to measure any optical activity in a sample prepared by dissolving a large single crystal and thus tentatively conclude that resolution occurs only in domains.

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(18) Depending upon the mode of closure of **4** or the direction of addition to **5**, isomers of **6a**, with the ether oxygen syn or anti to the dienyl unit, can be produced. In fact, a minor isomer (5% yield) displaying spectral characteristics analogous to **6a** (the major isomer) can be seen in Figure 1B.

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(23) National Institutes of Health Trainee, 1974–present.

(24) Camille and Henry Dreyfus Teacher–Scholar Grant Awardee 1972–1977.

Jane Berkowitz Carlton,[23] Ronald H. Levin*
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Jon Clardy*[24]
Ames Laboratory—USERDA and Department of Chemistry
Iowa State University
Ames, Iowa 50011

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Ion Structure Determination by Gas Phase Derivatization and Collisional Activation Mass Spectrometry[1]

Sir:

Structural studies of gaseous organic ions have commonly employed characterization by ion-molecule reactions,[2,3] especially utilizing ion cyclotron resonance (ICR) spectrometry,[4-6] and by metastable[7,8] and collisionally activated[9] decompositions occurring in a field-free drift region of the mass spectrometer. Collisional activation (CA) spectra are uniquely insensitive to differences in ion internal energies, and have been found applicable in a wide variety of problems.[1,9,10] However, for particular ions, especially those without functional groups, the CA spectra of isomers can be closely similar; further, isomerization may occur in the relatively long times (CA, $\sim 10^{-5}$ s; ICR, $> 10^{-3}$ s) before structural assay.[11] We report here that it is possible to alleviate these disadvantages by in situ derivatization of the newly formed ions using ion-molecule reactions, followed by characterization of the products from their CA spectra; the isomeric $C_4H_9^+$ ions I-IV (heat of formation,[12] kcal/mol, in parentheses)

$CH_3CH_2CH_2CH_2^+$ I(ΔH_f = 201)

$(CH_3)_2CHCH_2^+$ II (ΔH_f = 199)

$C_2H_5(CH_3)CH^+$ III (ΔH_f = 183)

$(CH_3)_3C^+$ IV (ΔH_f = 167)

have been investigated using this technique.

$C_4H_9^+$ ions generated from any of the isomeric halobutanes apparently undergo metastable decomposition (lifetimes $\sim 10^{-5}$ s) from a common structure, or mixture of structures.[8]

Table I. Partial CA Spectra[a] of $C_6H_{11}O^+$ from Isomeric $C_4H_9^+$ Ions

	Butyl bromide precursor			
m/e	*n*-	iso-	*sec*-	*tert*-
27	11.3	7.9	9.7	8.9
29	7.2	6.5	7.9	8.1
39	15.5	17.1	14.1	25.6
41	13.8	14.2	11.4	20.4
56	7.3	10.4	8.1	12.9
58	2.6	3.7	1.0	7.8

[a] Abundances relative to the total ion abundance of the 17 peaks in the CA spectra, not including six peaks from metastable decomposition; no measurable change at ~14 eV ionizing electron energy.

However, ions from *n*-butane and isobutane show different ion-molecule reactivities at high source pressures (lifetimes $\sim 10^{-7}$ s).[2] In ICR studies of ions from haloalkanes,[5] only I and III yield $C_8H_{11}^+$ from reaction 1 with furan,[13]

$$C_4H_9^+ + C_4H_4O \xrightarrow{k_1} C_8H_{13}O^+ \longrightarrow C_8H_{11}^+ \qquad (1)$$

consistent with the isomerization I → III observed in solution studies;[14] in contrast, only I and II undergo ICR reaction with CH_3COOH. In radiolysis studies[15] (ion lifetimes $<10^{-8}$ s) III ions were found to rearrange to IV, the extent increasing with increasing internal energy. Hydrogen scrambling in IV ions was found to proceed through an "isobutyl-ion-like" transition state without III formation,[15] although other studies[16] indicate that II ions rearrange to a 1:4 mixture of III and IV.

Although the initial $C_4H_9^+$ ions from electron ionization of the isomeric bromobutanes should have structures I-IV,[15] their CA spectra are very similar (±5% abundance deviation). The CA spectra of the $C_8H_{13}O^+$ ions from reaction 1 with furan are the same for I, II, and III as precursors, but differ significantly from the spectrum of the product with IV. However, the CA spectrum of $C_8H_{13}O^+$ ions formed from a 1:1 mixture of *sec*- and *tert*-butyl bromide is the same as that from III alone, indicating for reaction 1 that k_1 (IV) $\ll$ k_1 (III).

The $C_6H_{11}O^+$ ions[5,13] from reaction 2 do show substantial differences in their CA spectra (Table I).[17,18]

$$C_4H_9^+ + CH_3COCl \xrightarrow{k_2} C_6H_{11}O^+ + HCl \qquad (2)$$

The spectra of III and IV are consistent with minimal isomerization in $\sim 10^{-6}$ s; the III ions, although of higher ΔH_f, must contain <15% IV, based on the abundance of *m/e* 58. The spectral differences should not arise from k_2 variations caused by differences in ion internal energy, as the CA spectra are independent of the energy of the ionizing electrons. The CA spectrum of I agrees within experimental error with that of a ~6:1 mixture of III:IV,[19] consistent with the facile isomerization of I → III observed previously.[2,8,14] The tendency for II to isomerize should resemble I, and the data indicate that II is also a mixture of III and IV ions. To measure [III]/[IV] more accurately, it was necessary to prepare a calibration curve (Figure 1) because k_2 (III) and k_2 (IV) have different values; from this the abundance values for *m/e* 56, 29/41, and 31/43 all indicate similar ratios of III and IV. Without knowledge of the CA spectrum of pure II an upper limit cannot be placed on the amount of nonisomerized II; if this is low, as expected,[16] our results indicate that II isomerizes to a 2.6:1 mixture of III:IV.[20] As suggested by Jennings,[5] the observation that the ICR reactivities of I and II are different than those of III and IV appears to arise from differences in ion internal energy,[5] a drawback of ICR evidence for ion structure.[4]

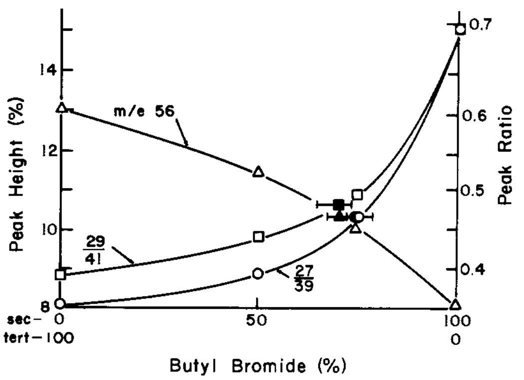
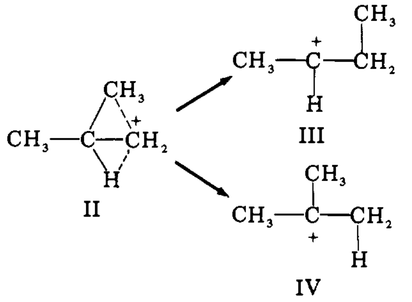


Figure 1. Plot of the relative abundances of peaks in the CA spectra of $C_6H_{11}O^+$ ions produced by reaction of CH_3COCl and $C_4H_9^+$, vs. the composition of a mixture of *sec*- and *tert*-butyl bromide used to produce the $C_4H_9^+$ ions. Filled symbols: values for corresponding peaks in the CA spectrum of $C_6H_{11}O^+$ ions from isobutyl bromide and CH_3COCl. Values are averages of four spectra, determined separately from those of Table I.

The predominant formation of III in the gas phase isomerization of II rules out II as the transition state for IV isomerization,[15] and is in contrast to the predominant solution isomerization[16] of II to IV. Very recent results[21] indicate that the enthalpy difference for III → IV is the same in solution and gas phases; thus the pathway favored for the lowest energy conformation of II may be more important in the absence of ion solvation (eq 3).



(3)

Acknowledgment. We are grateful to Dr. T. Wachs and F. M. Bockhoff for instrumental and experimental contributions, to Dr. B. K. Carpenter for stimulating discussions, and to the National Institutes of Health (Grant GM-16609) for generous financial support.

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composition of $C_6H_8D_3O^+$ formed from CD_3COCl gives $C_2D_3O^+$, not $C_2H_3O^+$.

(18) Measurements were made with instrumentation described previously,[1,9,10] 7.8 kV ion accelerating potential. The ion source was modified for higher pressure ($\sim 10^{-2}$ Torr) operation,[1] with pressure (reagent)/pressure (butyl bromide) = 50–100.

(19) Ca. 10% of an isomer other than III or IV is possible; CA spectra of the products of ions from I reacting with furan (reaction 1) and with CH_3COOH are also nearly identical with the spectra from III.

(20) Since completion of this work, an improved computer data acquisition system has been installed. Remeasurement of the CA spectra of I–IV (*without* derivatization) with ±1% precision gave data consistent with these conclusions; a computer error minimization program finds the II spectrum (13 peaks) corresponds to 75% (±20%) III and 25% IV.

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Paul P. Dymerski,[22] F. W. McLafferty*
Department of Chemistry, Cornell University
Ithaca, New York 14853

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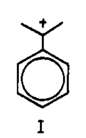
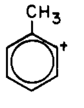
Benzyl Cation. A Long-Lived Species in the Gas Phase?

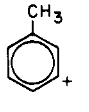
Sir:

Considerable attention has been focused in recent years on providing evidence for or against the stable existence of the benzyl cation (I) in the gas phase. Most recent are investigations by McLafferty and Winkler[1] and by Dunbar and coworkers.[2] The former authors have measured the collisional activation mass spectra of a large number of compounds leading to ions of formula $C_7H_7^+$ and have concluded that in addition to tropylium (II), presumably the lowest energy form, a number of other isomers exist for at least 10^{-5} s. These include the benzyl cation as well as a number of other species (III–VI) of lesser stability. In one series of experiments Shen, Dunbar, and Olah[2a] investigated the distribution of isotopically related product ions in the reaction $C_7H_7^+$, generated in an ion cyclotron resonance spectrometer by electron impact of toluene, with labeled toluene.

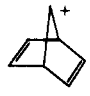

I


II


III

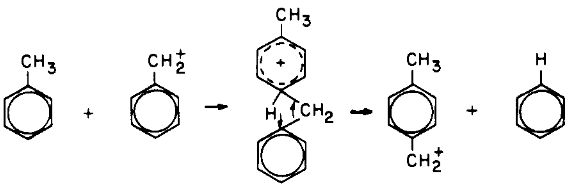

IV


V


VI

$$C_7H_7^+ + C_6H_5CH_3 \longrightarrow C_8H_9^+ + C_6H_6 \qquad (1)$$

From their results with $C_6H_5CD_3$ and $C_6D_5CH_3$, these authors concluded "that of the nine hydrogens in the $C_8H_9^+$ product, three come from the methyl group of neutral toluene, four come from the ring of neutral toluene, and two are drawn in a scrambled fashion from the $C_7H_7^+$ reactant, with some preference to the hydrogens originally on the methyl group". The fact that only two of the product ion's hydrogens originate from $C_7H_7^+$ and that scrambling, although extensive, is incomplete, led Shen, Dunbar, and Olah to propose the following mechanism involving a benzyl cation (eq 2). Shortly thereafter, Dunbar[2b] demonstrated that $C_7H_7^+$, formed in an ICR spectrometer by photodissociation of toluene parent ion, quickly resolves itself into two populations of markedly different reactivity. He assigned the less reactive to tropylium, the more to the benzyl cation.

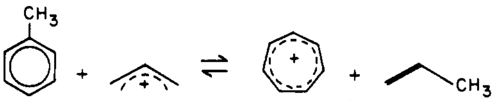


(2)

It appears, therefore, that while there exists substantial evidence in favor of the benzyl cation as a long-lived entity in the gas phase, little is known from experiment about the details of its structure or about its thermochemical stability relative to that of tropylium. It is to these questions that we address ourselves in the present communication. Using pulsed ion cyclotron resonance (ICR) spectroscopy[3] we have established at long times (≤2 s) chemical equilibrium involving transfer of the halide anion between benzyl and *tert*-butyl chloride. The measured free energy for eq 3 at 303 K ($\Delta G° = 0.18 \pm 0.10$ kcal/mol)[4] is in accord with Beauchamp's observation[5] that bromide anion transfer from benzyl to *tert*-butyl bromide is thermoneutral or slightly exothermic. Assuming $\Delta H_f°(298)$ for the *tert*-butyl cation to be 169 kcal/mol,[6,10] we arrive at a value of 217.2 kcal/mol for the heat of formation of $C_7H_7^+$ derived from benzyl chloride.[11] This is higher than previously reported heats for either the benzyl cation (213 kcal/mol[12]) or for tropylium (209 or 212 kcal/mol).[13,14]

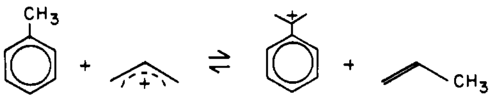
$$C_6H_5CH_2Cl + (CH_3)_3C^+ \rightleftharpoons C_7H_7^+ + (CH_3)_3CCl \qquad (3)$$

In order to clarify the situation with regard to the relative stabilities of the benzyl and tropylium cations, we have determined theoretically their heats of formation by way of ab initio molecular orbital calculations at the split valence shell, 4-31 G level.[15] In particular we have calculated the energetics of the hydride transfer reactions in eq 4 and 5, involving comparison of the benzyl and tropylium cations, respectively, to the allyl cation, a species of similar electronic structure.



(4)

ΔE(4-31G) = −16.0 kcal/mole



(5)

ΔE(4-31G) = −25.2 kcal/mole

Combining these results with the experimental $\Delta H_f°(298)$ for the allyl cation (226 kcal/mol),[12,20] we arrive at theoretical estimates of 217.1 and 207.9 kcal/mol for the heats of formation of benzyl and tropylium, respectively.[21] The first, involving benzyl cation, is in good accord with the experimental heat calculated for the ion resulting from halide abstraction from benzyl chloride; the second is not. Although our theoretical estimate of the heat of formation of the benzyl cation is some 4 kcal/mol higher than the value obtained by Lossing,[12,22] that corresponding to tropylium is in reasonable agreement with the lower of the two experimental determinations.[13]

To further substantiate that it is the benzyl rather than tropylium cation which is actually being observed in the ICR spectrometer, we have measured the free energy of eq 2 at a second (elevated) temperature. Recalling the definition of the free energy

$$\Delta G° = \Delta H° - T\Delta S°$$

it follows that

$$\Delta S° = (\Delta G°_{T_1} - \Delta G°_{T_2})/(T_2 - T_1) \qquad (T_2 > T_1)$$

Assuming that $\Delta S°$ is itself largely temperature independent, we can see that obtaining $\Delta G°$ at two different temperatures gives us the entropy change. To a first approximation $\Delta S°$ may