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Isomerization of Gas-Phase Hydrocarbon Ions. Radical Trapping. 3

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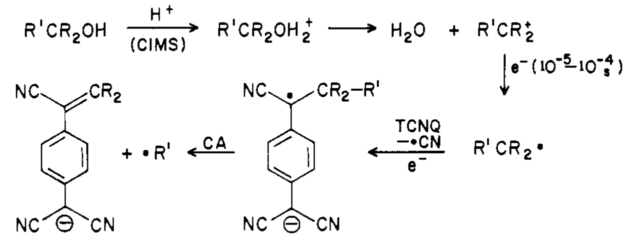
Abstract: Carbon-centered radicals, produced in a chemical-ionization plasma by ion-electron recombination, are trapped in a fast gas-phase reaction with tetracyanoquinodimethan and the products of this reaction, after ionization by electron capture, are analyzed, using mass selected collisional activation mass spectrometry. The structures of the ions at the instant of neutralization, 10^{-5}–10^{-4} s after formation, are determined from the collisional activation results. Isomerization occurring in selected $[C_nH_{2n-1}]^+$, $[C_nH_{2n+1}]^+$, and $[C_nH_{n+(n-7)}]^+$ ions, $n \leq 9$, have been delineated and the results compared to previously published gas-phase and/or solution results.

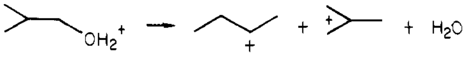
A number of approaches are available for determining the structure of gas-phase ions. These include determining the heats of formation of the ions,[1] investigating ion–molecule reactions,[2] and analyzing ion-dissociation products by (a) intensity ratios in metastable ion dissociation,[3] (b) translational energy release in metastable ions,[4] and (c) intensity ratios in collisional activation decompositions.[5] The above techniques are comparative in nature.

The preceding paper[6] describes an interpretive technique (RTCA) for determining gas-phase radical structures. The technique, modified to determine ion structures, is hereafter referred to as IRTCA (ion/radical-trapping collisional activation). Scheme I shows the nature of the IRTCA technique. An even-electron positive ion is produced by dehydration of a protonated alcohol; under chemical ionization (CI) conditions many of the ions will be neutralized by electron capture. The ensuing radicals are captured in a fast reaction with 7,7,8,8-tetracyanoquinodimethan (TCNQ), and the resulting compounds are ionized and mass selected by using the magnetic sector of the mass spectrometer and then collisionally fragmented in a gas-collision cell. The electric sector is scanned over the appropriate potentials to pass the parent and the collisionally induced fragment ions, thus creating a collisional activation (CA) mass spectrum of the parent ion.

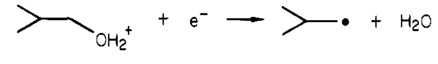
Scheme I



As noted in the preceding paper,[6] the only significant fragment ions observed from collisional decomposition of the $[TCNQCR_2R' - CN]^{-}\cdot$ ions are loss of H, a small loss of HCN, and major peaks for the loss of the R groups. Thus, the structures of even-electron positive hydrocarbon ions in a CI source can be determined if the radicals produced from ions by ion neutralization processes are representative of the ion structures, and if radicals of the same nominal mass as the ions are not produced by other mechanisms. Alkyl ions can be produced from protonated alcohols via eq 1, with no evidence of direct formation of alkyl radicals of the same mass. However, radicals of the same mass as the ions might be formed by neutralization of the MH$^+$ ion followed by loss of water (eq 2). For C$_4$ and larger alcohols the $[MH - H_2O]^+/MH^+$ ratio is ca. 20, thus radical formation by eq 2 is expected to be relatively unimportant, except possibly in the propanol case where the ratio is ca. 1. Production of alkyl radicals from amines by a process similar to that in eq 3 is not important, as determined from the radical–TCNQ trapping reaction, even when MH$^+$ is the dominant ion in the positive-ion mass spectrum. By analogy this should not be an important mechanism for radical formation in alcohols.

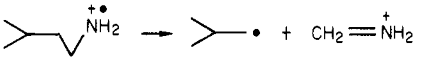


(1)



(2)

A comparison of the IRTCA spectrum of 2-methyl-1-propanol and the RTCA spectrum of isopentylamine shows that butyl radical production by mechanisms other than butyl-ion neutralization is not important for 2-methyl-1-propanol. Isobutyl radicals are produced directly by the fragmentation of the isopentylamine molecular ions (eq 3), whereas dehydration of protonated 2-methyl-1-propanol produces C$_4$H$_9$$^+$ ions (eq 2). The isopentylamine CA data show dominant retention of the primary butyl structure. (The ratio for losses of $\cdot CH_3$, $\cdot C_2H_5$, and $\cdot C_3H_7$ is 0.6:0.2:10; loss of $\cdot CH_3$ is expected for tertiary, $\cdot CH_3$ and $\cdot C_2H_5$ in a 1:1.85 ratio for secondary, and $\cdot C_3H_7$ for primary butyl radicals.) However, the IRTCA spectrum from the 2-methyl-1-propanol plasma indicates almost exclusive capture of tertiary and secondary butyl radicals by TCNQ (the ratio for the above losses is 10:1.7:0.4, respectively). These results are consistent with the hypothesis that the $\cdot C_4H_9$ radicals trapped in the CI(N$_2$/2-methyl-1-propanol/TCNQ) plasma were produced from ions which isomerized prior to neutralization. Similar results were obtained for neopentyl alcohol.



(3)

Because ion–electron recombination is a Franck–Condon process and is equally rapid for isomeric ions, the initial radical structures produced will be representative of the ion structures present in the CI source. Most of the radicals produced by neutralization have sufficient energy to decompose before undergoing a stabilizing collision. These smaller radicals are rejected in the mass selection process of the IRTCA technique, so that only those radicals formed with insufficient energy to fragment before a stabilizing collision occurred were sampled. Most of the radical structures produced from ions in this study had carbon chain lengths too short for radical isomerization to occur by intramolecular hydrogen transfer through five-membered and larger cyclic transition-state structures. Comparison of the IRTCA data with previous studies of gas-phase

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ion structures strongly suggests that higher-energy radical-isomerization processes (such as smaller transition-state configurations) are not important. Thus, the IRTCA technique appears well suited to the determination of "stable" gas-phase ion structures.

For this work even-electron positive hydrocarbon ions were usually produced from alcohols and occasionally from alkyl halides. The average lifetime of the ions before neutralization is estimated to be ca. 10^{-5}–10^{-4} s. Under CI conditions this is sufficient time for the ions to undergo enough collisions to be in near thermal equilibrium with the surrounding gases. Because ion structures often depend on both internal energy and lifetimes, techniques which sample ions in different energy and time regimes might be expected to produce somewhat different results from those reported here.

Experimental Section

The techniques, instrumentation, and calculations used in the quantitative determination of gas-phase ion structures are identical with those reported in the preceding paper on radical-structure determinations,[6] except that alcohols and alkyl halides, which, when protonated, produce alkyl ions directly by fragmentation, were used instead of radical-producing amines and ketones. The alcohols and alkyl halides were obtained from a Chem Service, Inc. (Media, Pa.), Lab Assist Kit or from Aldrich Chemical Co. and were used without further purification.

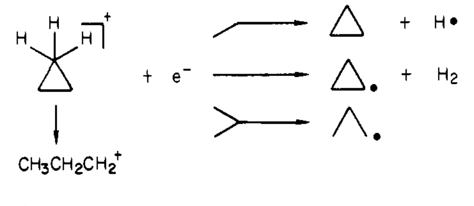
Results and Discussion

$C_3H_7^+$ Ions. Considerable effort has been devoted to elucidating the structures of $C_3H_7^+$ ions. Theoretical,[8-10] solution,[11,12] and gas-phase[13-16] studies have concluded that the *sec*-propyl ion is the most stable form of $C_3H_7^+$. Nevertheless, scrambling of the hydrogen and carbon atoms in this ion has been observed in solution and in the gas phase. A combination of deuterium and carbon-13 labeled *sec*-propyl ions in solution show that hydrogen scrambling is slightly faster than carbon scrambling.[17] These results were interpreted to suggest that interconversion between primary and *sec*-propyl ions via a 1,2-hydride shift is of comparable energy to the process of carbon scrambling through a c-$C_3H_7^+$ structure. On the other hand, the available gas-phase data suggest that conversion of c-$C_3H_7^+$ to *sec*-$C_3H_7^+$ is fast (10^{-7} s)[18] but conversion of primary $C_3H_7^+$ to *sec*-$C_3H_7^+$ is relatively much slower.[19,20]

Gas-phase studies in which the initially formed $C_3H_7^+$ ions might be expected to have a primary structure show the presence of two $C_3H_7^+$ structures after 10^{-6} s. In all cases, the dominant ion had the *sec*-$C_3H_7^+$ structure, and the minor $C_3H_7^+$ ion has either a cyclic or a primary structure.[19-21] Although evidence for a stable c-$C_3H_7^+$ ion has been reported,[14,15] collisional activation analysis suggests that c-$C_3H_7^+$ isomerizes to *sec*-$C_3H_7^+$ within 10^{-6} s.[18]

IRTCA results for $C_3H_7^+$ ions produced by dehydration of protonated 2-propanol in the CI(N_2/2-propanol/TCNQ) plasma show by dominant loss of $\cdot CH_3$ from $[TCNQC_3H_7 - CN]^{-\cdot}$ ions that *sec*-$C_3H_7^+$ ions retained the secondary structure. On the other hand, 1-propanol predominately isomerized to the secondary structure (65 ± 5%), but some radicals having a primary structure (35 ± 5%) were trapped as shown by the relative intensities of the $\cdot CH_3$ and $\cdot C_2H_5$ losses (10:5.4) in the IRTCA spectrum. However, primary propyl radicals may be produced by the mechanism shown in eq 2, making a quantitative discussion meaningless in this case.

The IRTCA spectrum of protonated cyclopropane was very similar to that of 2-propanol, showing a ratio of secondary to primary $C_3H_7^+$ of 10:0.7. These results do not provide information concerning the presence of c-$C_3H_7^+$ at the time of neutralization, because protonated cyclopropane is expected to react by eq 4–6 upon recombination with an electron. The presence of a small amount of primary $\cdot C_3H_7$ radicals may be the result of eq 6, or ring opening of the protonated cyclopropane ion to the primary ion which captures an electron to produce the primary radical.



(4)
(5)
(6)

Addition of $\cdot C_3H_5$ to TCNQ was observed, and collisional decomposition of the $[TCNQC_3H_5 - CN]^{-\cdot}$ ions resulted only in loss of H, suggesting a cyclic $\cdot C_3H_5$ structure. However, the amount, if any, of $\cdot C_3H_5$ produced via eq 5, as compared to hydrogen abstraction (eq 7), is not known.

$$C_3H_6^{+\bullet} \text{ or } TCNQ^{+\bullet} + c\text{-}C_3H_6 \longrightarrow C_3H_7^+ \text{ or } TCNQH^+ + \triangle\bullet \quad (7)$$

$C_4H_7^+$ Ions. An intriguing mechanistic problem in carbonium ion chemistry has been to define the nature of the intermediate(s) involved in the rapid equilibration of the cyclopropylcarbinyl, cyclobutyl, and homoallyl cations.[22] Considerable information is available concerning these ions in solution,[23,24] but relatively little gas-phase data exist. The available gas-phase results show the existence of the cyclopropylcarbinyl cation,[25] in agreement with STO-3G calculations suggesting that this ion is the most stable form of $C_4H_7^+$.[26] Gas-phase results also show that cyclopropylcarbinyl and cyclobutyl ions coexist after 10^{-9} s.[27]

The ratio for losses of H, $\cdot CH_3$, C_2H_4, and $\cdot C_3H_5$ in the IRTCA spectra of the $C_4H_7^+$ ions from both cyclopropylcarbinol and bromocyclobutane was 10:2.8:8.0:7.5. Thus, an identical mix of $C_4H_7^+$ ions was present in the CI source after ca. 10^{-5}–10^{-4} s regardless of whether the initial ions had the cyclobutyl or cyclopropylcarbinyl structure.

The loss of $\cdot C_3H_5$ in the IRTCA spectrum shows that a major portion of the $\cdot C_4H_7$ radicals that attached to TCNQ had a primary structure, suggesting that the precursor of the $\cdot C_4H_7$ radicals was the homoallyl or cyclopropylcarbinyl ions.[28] The amount of cyclobutyl ions present after 10^{-5}–10^{-4} s cannot be

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Table I. Butyl Ion Isomerization as a Function of the Partial Pressure of the Butyl Ion Precursor

		percentage of		
precursor	partial pressure of precursor[a]	primary	secondary	tertiary
1-bromobutane	4.0×10^{-6}	19	72	9
	1.5×10^{-5}	19	60	21
	4.0×10^{-5}	17	44	39
	5.5×10^{-5}	18	35	47
1-butanol	2.5×10^{-6}	10	82	8
	5.0×10^{-5}	13	55	32
	6.0×10^{-5}	13	49	38
2-methyl-1-propanol	7.0×10^{-6}	3	19	78
	1.0×10^{-5}	3	18	79
	3.5×10^{-5}	3	5	92
2-bromobutane	1.0×10^{-6}	0	>98	<2
2-butanol	2.0×10^{-6}	2	90	8
	1.0×10^{-5}	2	87	11
	4.0×10^{-5}	0	84	16
2-methyl-2-propanol	$4\text{–}40 \times 10^{-6}$	0	0	100

[a] Measured by the Bayard–Alpert gauge in the source housing.

precisely determined; collisional decomposition of $[TCNQC_4H_7 - CN]^{-}\cdot$ ions produced from cyclobutyl radical addition to TCNQ according to Scheme I is expected to lose only hydrogen atoms, but hydrogen atoms are also lost from these ions by unimolecular decompositions. The ratio for $\cdot H$, $\cdot CH_3$, $\cdot C_2H_4$, and $\cdot C_3H_5$ losses, corrected for metastable hydrogen-atom loss, is estimated to be 7.1:3.5:10:9.4. Ignoring the unusual C_2H_4 neutral loss, for which we have no explanation, the calculated contributions are 36 ± 10% cyclobutyl, 47 ± 10% homoallyl or cyclopropylcarbinyl, and 17 ± 10% tertiary methylcyclopropyl or secondary allyl ions.

C_4H_9 Ions. In solution, the isomeric butyl fluorides in SbF_5[29] and the butyl alcohols in SbF_5–HSO_3–SO_2[30] produce butyl ions which isomerize to the *tert*-butyl structure. The situation in the gas phase is not so clear. For example, metastable and CA studies of $C_4H_9^+$ ions generated from different precursors show that the butyl ions have isomerized to a common structure (presumably tertiary) or mixture of structures before fragmentation.[31-33] On the other hand, ionization potential (IP) and appearance potential (AP) measurements,[34] radiolysis experiments,[21] ion–molecule studies,[35,36] and ion cyclotron resonance (ICR) studies[37] show that isomeric butyl ions do not isomerize to a common structure or common mixture of structures.

Dymerski and McLafferty calculated the degree of isomerization of butyl ions generated from the isomeric butyl bromides in a CA experiment in which the butyl ions were derivatized by ion–molecule reactions with CH_3COCl and the products collisionally fragmented.[36] Primary *n*-butyl ions isomerized to a 6:1 mixture of *sec*- and *tert*-butyl ions, and primary isobutyl ions isomerized to a 75% (±25%):25% mixture of *sec*- and *tert*-butyl ions, respectively. Less than 15% of the *sec*-butyl ions rearranged to a tertiary structure. However, a later ICR study by Shold and Ausloos found that isobutyl ions generated from isobutyl bromide isomerize exclusively (±5%) to the tertiary structure within 10^{-3}–10^{-1} s. The ratio of secondary (and possibly primary) to tertiary structures generated from *n*- and *sec*-butyl bromides was found to be influenced by changes in the partial pressure of propyl bromide, but not by the presence of formaldehyde. The much higher conversion to the *tert*-butyl structure with increased propyl bromide partial pressure was thought to occur through a transient dialkylhalonium ion.[37]

The contradictory nature of some of these results can in part be explained by the different internal energies and lifetimes of the sampled ions. For example, butyl ions with sufficient internal energy to lose methane in metastable decompositions apparently rearranged to the tertiary butyl structure prior to decomposition. Likewise, the CA results from underivatized butyl ions can be explained by assuming rearrangement to the tertiary structure occurs *after collision* and before fragmentation. However, the reported differences in the relative amounts of the secondary and tertiary structures generated from the derivatized isobutyl cation is probably due to misinterpretation of the results in the CA study.

The results from the IRTCA study are given in Table I and reaffirm several points made in earlier work. For example, *sec*-butyl ions were found to remain predominately secondary, ca. 100% at low 2-butanol or 2-bromobutane pressures, but at higher pressures the relative amount of tertiary structure increased to ca. 15%. A more pronounced change in the relative amounts of secondary and tertiary butyl structures was found for the rearrangement of the primary *n*-butyl ions produced from 1-butanol or 1-bromobutane. At the lowest partial pressure of 1-bromobutane (ca. 0.06 torr), a ratio of 9:1 was observed for secondary relative to *tert*-butyl ions, and at the highest 1-bromobutane pressure (ca. 0.8 torr), the ratio was 0.76:1. A similar but less pronounced increase in the relative tertiary ion concentration was observed when the 1-butanol pressure was increased a like amount. Interestingly, an increase in the nitrogen gas pressure at constant bromobutane or butanol pressure had no effect on the *sec*-:*tert*-butyl ion ratio. The variation in the observed degree of isomerization with partial pressure of 1-bromobutane is consistent with the ICR study.[37]

The IRTCA results indicate that the isobutyl ion rearranges predominantly to the tertiary structure, also in agreement with the ICR study. Consistent with this study are the IRTCA results showing that the relative amount of secondary to tertiary structures for this ion varies from 1:4 at ca. 0.2 torr to 1:18 at ca. 0.6 torr of 2-methyl-1-propanol. A value of 3% primary ion remaining after $>10^{-5}$ s was found for all experiments, but since this value is within the ±5% error window we estimate for these results, it may not be significant.

The results obtained from the ionization of 1-bromobutane and 1-butanol indicate that primary butyl ions can survive for $>10^{-5}$ s in the CI source. The $[MH - H_2O]^+/MH^+$ ratio in the positive ion mass spectrum of 1-butanol is too high to account for the primary radicals via eq 2. The small changes in the relative concentration of the primary butyl ions with pressure in the CI source were within the error limit of any single experiment, but over a number of experiments the percentage of primary ions observed ranged from 5–13% with 1-butanol as precursor and 8–18% with 1-bromobutane. Within the limitations of this technique, no evidence was found that either *sec*- or *tert*-butyl ions revert to high-energy structures.

$C_nH_{2n-1}^+$ Ions ($n = 5$–7). In SbF_5–SO_2ClF solution a single proton magnetic resonance line at δ 4.68 is observed for the cyclopentyl ion at temperatures as low as −70 °C, which has been interpreted as suggesting a rapidly equilibrating secondary cyclopentyl structure.[38] Under similar conditions,[38,39] and in the gas phase,[40,41] cyclohexyl ions isomerize to the *tert*-methylcyclopentyl ion.

The gas-phase fates of the cyclohexyl and cyclopentyl ions, determined by using the IRTCA technique, parallel the solution results. The CA spectrum of the $[TCNQC_6H_{11} - CN]^{-}\cdot$ ions produced in the CI(N_2/cyclohexanol/TCNQ) plasma showed

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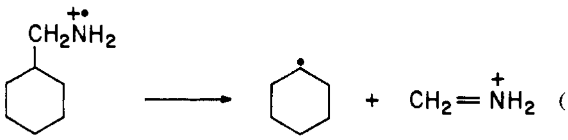
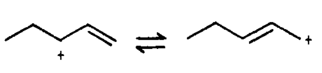
losses of ·H, $·CH_3$, $·C_2H_5$, $·C_3H_7$, $·C_4H_9$, and $·C_5H_9$ in the ratio of 10:10:2:2:1:0.2, respectively. These results can be compared to the CA results from $[TCNQC_6H_{11} - CN]^{-}·$ ions produced in the $CI(N_2$/(aminomethyl)cyclohexane/TCNQ) plasma, where the dominant C_6H_{11} radicals have the cyclohexyl structure (eq 8), and the ratio for the above losses is 10:0.3:0.3:1.3:0.7:0.3,


(8)

respectively, showing dominant loss of hydrogen atoms. The H· loss in the IRTCA spectrum of the cyclohexyl ion suggests that only 10 ± 10% retained the cyclic structure. The dominant $·CH_3$ alkyl radical loss in the IRTCA spectrum strongly suggests that the most prominent gas-phase ion structure (62 ± 10%) is the *tert*-methylcyclopentyl ion, in agreement with solution and gas-phase studies. The remaining losses can be explained by assuming that all possible open-chain allylic radicals are produced and that the dominant fragmentations of the $[TCNQC_6H_{11} - CN]^{-}·$ ions are directed so that bond breakage adjacent to the double bond is strongly disfavored (except for the primary radical/TCNQ addition products where fragmentation adjacent to the double bond must compete with C–H bond cleavage).

The losses of ·H, $·CH_3$, $·C_2H_5$, $·C_3H_7$, and $·C_4H_7$ in the CA spectrum of $[TCNQC_5H_9 - CN]^{-}·$ ions produced in the CI(N_2/chlorocyclopentane/TCNQ) plasma are in the ratio of 10:1:5:1.2:0.5, respectively. The ratio for ·H loss to major alkyl losses suggests 45 ± 10% retention of the secondary cyclopentyl structure. The major $·C_2H_5$ alkyl loss can be explained by assuming isomerization of the $C_5H_9^+$ ion to structures **1** or **2**. However, an actual sample of **1** (produced in the CI plasma from protonated 1-penten-3-ol) gave a very different IRTCA spectrum in which the ratio of H, $·CH_3$, $·C_2H_5$, $·C_3H_5$, $·C_3H_7$, $·C_4H_7$, and $·C_5H_7$ losses was 9.8:10:4.0:1.2:1.2:1.5:1.2, respectively. The fact that **1** undergoes major isomerization to a structure that predominately loses $·CH_3$ in the IRTCA spectrum suggests that **1** is not the major product of cyclopentyl-ion isomerization.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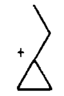
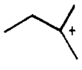

2

Comparison can also be made between the cyclopentyl cations and the $C_5H_9^+$ ions produced from cyclopropylmethylcarbinol. The cyclopropylmethyl cation can produce **2** by a 1,2-hydride shift. The IRTCA spectrum of the $C_5H_9^+$ ions from cyclopropylmethylcarbinol showed ·H, $·CH_3$, $·C_2H_5$, $·C_3H_5$, $·C_3H_7$, $·C_4H_7$, and $·C_5H_7$ losses in a ratio of 10:3.5:4.0:1.5:1.5:3.3:1.5, respectively. Loss of $·CH_3$ and $·C_3H_5$ is expected to arise from cyclopropylmethyl cations which did not isomerize. The loss of $·C_4H_7$ possibly suggests the presence of the primary cyclobutylcarbinyl cation. The remainder of the spectrum is similar to that observed for the cyclopentyl ion and may indicate that **2** and cyclopentyl ions rapidly equilibrate.

In contrast to the IRTCA results for the isomeric $C_5H_9^+$ ions, the IRTCA spectra of the $C_7H_{13}^+$ ions generated from 2-methylcyclohexanol, cyclohexylmethanol, and cycloheptanol yielded identical ratios of ·H, $·CH_3$, $·C_2H_5$, $·C_3H_7$, $·C_4H_9$, $·C_5H_{11}$, C_6H_{11}, and $·C_7H_{13}$ losses, namely 10:8.0:4.0:2.0:1.0:0.5:0.3:0.3. Clearly, a single structure cannot account for these results. The prominent losses of $·CH_3$ and $·C_2H_5$ can be explained if a major portion of the initial ions isomerize to the *tert*-methylcyclohexyl and *tert*-ethylcyclopentyl cations.

$C_nH_{2n+1}^+$ Ions ($n = 5$–8). Solution NMR studies of alkyl ions generated from C_5 and C_6 alcohols in FSO_3H-SbF_5-SO_2 solution show that these ions all have tertiary structures.[29,30] The isomeric pentanols upon protonation and loss of H_2O give the dimethylethylcarbonium ion (**3**), and protonated *n*-hexanol loses H_2O and isomerizes to the three *tert*-hexyl cations: the methyldiethylcarbonium ion (**4**), the dimethyl-*n*-propylcarbonium ion (**5**), and the dimethylisopropylcarbonium ion (**6**).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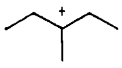
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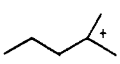
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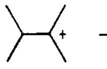
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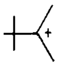
7

Early AP studies[42] inferred a secondary structure for gas-phase $C_5H_{11}^+$ ions generated from alkanes, but later studies using IP and AP measurements suggested that neopentyl and 2-pentyl ions isomerize to the tertiary structure.[43,44] Collisional activation studies[33,45] showed that most $C_5H_{11}^+$ ions (as well as $C_6H_{13}^+$ and $C_7H_{15}^+$ ions) produced by fragmentation of isomeric octanes had isomerized to a tertiary structure or mixture of structures at energies transferred by the collision process. $C_6H_{13}^+$ and $C_8H_{17}^+$ ions generated from primary, secondary, and tertiary halides were shown to have isomerized to a common structure before metastable fragmentation.[46] A series of studies using carbon-13 and deuterium labeling of heptyl iodides provides strong evidence that the heptyl ion rapidly isomerizes to the *tert*-butyldimethylcarbonium ion (**7**) prior to fragmentation.[47]

The IRTCA spectra for the isomeric pentyl ions show considerably more isomerization to the tertiary pentyl structure than was observed for the corresponding butyl ions. The $·CH_3$, $·C_2H_5$, $·C_3H_7$, and $·C_4H_9$ losses from collisional decomposition of the $[TCNQC_5H_{11} - CN]^{-}·$ ions produced in the CI(N_2/1-pentanol-/TCNQ) plasma were in the ratio 5.5:10:2.0:0.2, showing 15 ± 5% and 10 ± 5% isomerization to the secondary 2-pentyl and 3-pentyl ions, respectively, and 75 ± 5% isomerization to **3**. In the CI(N_2/3-methyl-1-butanol/TCNQ) plasma, these losses were in the ratio 5.0:10:0.1:0.2, demonstrating 92 ± 5% isomerization to **3** and 8 ± 5% isomerization to the secondary 3-pentyl ion. The ratio for these losses in the IRTCA spectrum of neopentyl alcohol was 5.0:10:0.2:1.0, showing 94 ± 5% isomerization to **3**. The same losses in the IRTCA spectrum of 3-pentanol were in the ratio of 6.0:10:3.0:0.1, showing 68 ± 5% isomerization to **3** and 21 ± 5% isomerization to the secondary 2-pentyl ion. This latter result is consistent with the isomerization of *sec*-butyl ions which showed less tendency to rearrange to a tertiary structure than did the primary butyl ions.

Hexyl ions produced from 2-ethyl-1-butanol and 1-hexanol gave, within the accuracy of the measurements, identical IRTCA spectra. The ratios for losses of $·CH_3$, $·C_2H_5$, $·C_3H_7$, and $·C_4H_9$ in the IRTCA spectra were 5.0:10:10:2.0, respectively. The loss of $·C_4H_9$ and a small part of the $·CH_3$ loss shows that 12 ± 5% of the hexyl ion current is from the secondary 2-hexyl ions. Based on the intensity of the remaining $·CH_3$ loss peak, ca. 50% of the ions were tertiary with 30 ± 10% having structure **4** and 20 ± 10% having structures **5** or **6**.[6] The remaining ions have the secondary 3-hexyl structure.

The amount of *sec*-hexyl relative to *tert*-hexyl ions is surprising, especially when compared to the relative amounts of secondary and tertiary butyl and pentyl ions produced from 1-hexanol and 1-pentanol, respectively. It is unlikely the results are in error because of direct hexyl radical production during ionization; however, assigning structures based on the IRTCA data becomes increasingly difficult as the alkyl chain lengths become longer. The fragmentation pathway factors used to calculate relative alkyl radical losses become less certain and the fragment ion intensity resulting from a single structure is reduced because of the greater number of structures; this combined with the increased number of calculations necessary to assign structure reduces the confidence in the relative percentages quoted.[6]

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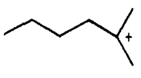
The IRTCA data for the heptyl ions produced from 1-heptanol are complex and the uncertainty in the calculated results is quite large. The ratio for loss of $\cdot CH_3$, $\cdot C_2H_5$, $\cdot C_3H_7$, $\cdot C_4H_9$, $\cdot C_5H_{11}$, and $\cdot C_6H_{13}$ is 5.1:10:6.0:4.5:3.5:0.5, which translates to <2% primary heptyl ions, 15 ± 5% secondary 2-heptyl ions, and 83 ± 15% tertiary heptyl ions. The calculations indicate 28 ± 15% **7** and **8**, 34 ± 15% **9**, and 21 ± 15% **10**. The IRTCA results are clearly not in agreement with reports that show complete isomerization of *n*-heptyl ions to **7**.[33,47] The lower internal energy of the ions sampled by the IRTCA technique, as compared to the previous studies in which only ions with sufficient energy to fragment were observed, probably accounts for the different results.



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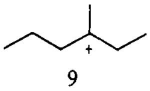

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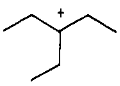
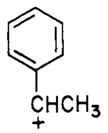


10

The Phenonium Ion. The ^{13}C and proton NMR spectra of an SbF_5SO_2ClF/2-phenylethyl chloride solution showed the presence of both the phenonium ion (**11**) and the α-phenylethyl ion (**12**).[48] Upon quenching the solution with a slurry of water in SO_2ClF at −78 °C, the only identifiable products were the 1- and 2-phenylethyl chlorides in a 1:3 ratio. The formation of **11** as an intermediate in the solvolysis of 2-phenyltosylate has also been suggested.[49]

Aryl participation in the expulsion of Br· from the molecular ion of 2-phenylethyl bromide has been suggested to occur in the gas phase leading to formation of **11**.[50] In a different study it was concluded from IP and AP measurements that **11** was not formed.[51] However, more recent CA results indicate that **11** is the dominant $C_8H_9^+$ ion produced from the 2-phenylethyl bromide molecular ion at low electron energies (near the threshold energy for fragmentation) and that **12** dominates at high electron energies.[52]

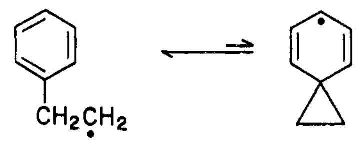
11



12

Because of the conflicting nature of the gas-phase results, the IRTCA spectrum of the $C_8H_9^+$ ions generated in the CI(N_2/2-phenylethanol/TCNQ) plasma was determined and compared to the IRTCA spectrum of the $C_9H_{11}^+$ ion produced from 3-phenylpropanol. The ratio of ·H, $\cdot CH_3$, $\cdot C_2H_5$, $\cdot C_3H_7$, $\cdot C_6H_5$, $\cdot C_7H_7$, and $\cdot C_8H_9$ losses from the $[TCNQC_8H_9 - CN]^{-}\cdot$ ions was 10:8.0:1.3:1.2:1.0:1.8:0.3. Under similar ion source and sample pressure conditions the same losses in the CA spectrum of the $[TCNQC_9H_{11} - CN]^{-}\cdot$ ions were in the ratio of 10:0.7:10:0.2:0.3:1.0:0.2. The IRTCA results for the $C_8H_9^+$ ions were pressure dependent, analogous to the *tert*-butyl results (Table I), so that as the partial pressure of 2-phenylethanol was increased, the ratio for losses of ·H, $\cdot CH_3$, and $\cdot C_7H_7$ changed from 10:8:1.8 to 10:6:4.

The major losses in the IRTCA spectra of $C_8H_9^+$ and $C_9H_{11}^+$ ions were $\cdot CH_3$ and $\cdot C_2H_5$, respectively, showing that the α-phenylethyl and α-phenylpropyl ions are the dominant $C_8H_9^+$ and $C_9H_{11}^+$ structures under the conditions of these experiments. However, the higher proportion of ·H loss relative to the major alkyl loss in the IRTCA spectrum of $C_8H_9^+$ ions compared to the spectrum of $C_9H_{11}^+$ ions suggests that some of the $C_8H_9^+$ ions had a secondary cyclic structure when neutralized. Additionally, loss of $\cdot C_7H_7$ from the $[TCNQC_8H_9 - CN]^{-}\cdot$ ions shows that a significant amount of primary β-phenylethyl radicals (**13**) was generated from $C_8H_9^+$ ions and captured by TCNQ, whereas essentially no primary γ-phenylpropyl radicals were captured in the 3-phenylpropanol ($C_9H_{11}^+$) CI plasma. These results can be explained by assuming that some of the $C_8H_9^+$ ions have structure **11**, which upon neutralization forms **14** as the secondary cyclic radical. **14** is known to rapidly rearrange to **13**[53] and could account for the presence of the primary radical. The CA results[52] suggest that primary $C_8H_9^+$ ions are stable for at least 10^{-5} s. Neutralization of these ions would also produce primary radicals.



13 **14**

Strong evidence that **11** and/or **14** is involved in the formation of the *primary* **13** radical is derived from the IRTCA results for the $C_8H_8D^+$ ions produced from 2-phenylethanol having a single deuterium on the C_1 position. The IRTCA spectrum shows approximately equal losses of $\cdot C_7H_7$ and $\cdot C_7H_6D$ from the primary radical, and therefore scrambling has occurred. However, $\cdot CH_2D$ instead of $\cdot CH_3$ was lost from $[TCNQC_8H_8D - CN]^{-}\cdot$ ions, produced from the *secondary* 1-phenylethyl radical, showing that **12** ions are not formed from **11**, and, once formed, are stable.

Conclusion

The products of the isomerization of a number of hydrocarbon ions having lifetimes of 10^{-5}–10^{-4} s have been determined quantitatively, using the IRTCA technique. These results are consistent with most gas-phase data for "stable" ions obtained by AP and IP measurements and by ion-trapping techniques. IRTCA data show that a significant percentage of primary *n*-butyl and possibly propyl, but not pentyl or hexyl ions, retain a primary structure. Changes in the partial pressure of the primary, and to a lesser extent the secondary, butyl ion precursors (e.g., bromobutane) changes significantly the relative amounts of secondary and tertiary butyl ions present in the mass spectrometer ion source. Additionally, isomerization of C_5 and larger alkyl ions was found to be more facile than isomerization of butyl and possibly propyl ions.

The IRTCA results are not in good agreement with solution or gas-phase metastable and CA results, especially for C_3 and C_4 alkyl ions. The discrepancies observed are probably related to the internal energy of the ions. In the metastable and CA techniques only ions with sufficient internal energy to fragment are observed. Apparently, alkyl ions will rapidly isomerize to the most stable structure(s) prior to fragmentation, even given the internal energies available from collisional activation.

The solution results are qualitatively similar to the CA and metastable results probably because the energy of the ions in solution allows isomerization to the more stable structures during the relatively long lifetime of the ions. The ion structures observed by using the IRTCA technique for the larger alkyl ions more closely resemble those in solution, suggesting that the critical energy for isomerization is lower for the larger ions, or that the internal energy imparted to the ions during formation is higher. Also in agreement with solution data is the indication from the IRTCA technique that phenonium ions (**11**) exist in the gas phase and do not interconvert with α-phenylethyl ions (**12**). The relative amounts of **11** and **12** produced in the ion source were found to be a function of the 2-phenylethanol pressure.

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