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Retention of Ring Structure in Cyclopentane and Alkylcyclopentane Molecular Cations

Sir:

In recent ion cyclotron resonance investigations, it was found that the photodissociation spectrum of the $C_5H_{10}^+$ ion formed by electron-impact ionization of cyclopentane coincided with that of $1\text{-}C_5H_{10}^+$ or $2\text{-}C_5H_{10}^+$, and it was concluded that cyclopentane ions quantitatively undergo ring opening.[1,2] In fact, upper limits of $<10^{-9}$ s have been suggested for the lifetime of alkyl-substituted cycloalkane molecular ions with 3-5-membered rings on the basis of a collisional activation and field ionization kinetic study.[3]

On the other hand, in an earlier gas phase radiolysis study,[4] it was demonstrated that only 20% of the parent ions from cyclopentane undergo ring opening to give *trans*-2-pentene (63%) and *cis*-2-pentene (37%) at a pressure of 20 torr. Furthermore, liquid phase radiolysis experiments indicated complete retention of the cyclic structure.[5] Here we are reporting experimental evidence which demonstrates that the apparent conflict can be resolved if one accepts, as is the case for cyclopropane and cyclobutane,[6] that the degree of ring opening in cyclopentane and alkylcyclopentane ions reflects the internal energy content of the molecular ions following the ionization process.

All measurements were taken with the NBS high-pressure photoionization mass spectrometer[7] operated, unless otherwise noted, at 292 K. The basic experimental approach involved the investigation of competitive charge exchange reactions occurring in cyclopentane-additive or alkylcyclopentane-additive mixtures (all API samples) in order to establish the fractional yields of cyclic ions. The additives were chosen to satisfy the following relationship involving ionization potentials (IPs): IP(cyclopentane) $\gg$ IP(additive) $\gg$ IP(olefinic isomers). When these criteria are met, the cyclic ion will undergo charge exchange with the additive, but the acyclic isomers will not. An obvious additional requirement was that the neutral components must not participate in any other ion-molecule reactions with either the cyclic or the olefinic ions derived from the particular neutral cyclopentane or the charge-exchange product. For example, cyclohexane's IP (9.88 eV)[8] is substantially lower than that of cyclopentane (IP = 10.50 eV)[8] and above those of any of the isomeric pentenes ($\leq$9.52 eV).[9] In a typical experiment, the fractional yield of $C_5H_{10}^+$ ions [defined as $I_{C_5H_{10}^+}/(I_{C_5H_{10}^+} + I_{C_6H_{12}^+})$] in a cyclopentane-cyclohexane mixture would be determined as a function of pressure in order to define that fraction of the $C_5H_{10}^+$ ions which did charge exchange with cyclohexane, i.e., that fraction which remained cyclic after ionization. Such data for two cyclopentane-cyclohexane mixtures following photoionization at 10.62 (curve A) and 11.7 eV (curve B) are given in Figure 1. Note that there are two regimes of essentially constant values for the fractional yields, at very low pressures in the reaction chamber, where collisions between $C_5H_{10}^+$ and cyclohexane are negligible, and at high pressures, where all of the cyclic $C_5H_{10}^+$ ions have reacted via charge exchange. The remaining fractional yield at higher pressures corresponds to the olefinic ions, which are unreactive toward cyclohexane. Consideration of the data from mixtures of various composition (2.5-10% cyclohexane) indicates that only 30 ± 2% of the $C_5H_{10}^+$ ions produced in the 11.7-eV photoionization of cyclopentane retain the cyclic structure contrasted with $\geq$96% of those formed at 10.62 eV. Charge exchange involving internally excited pentene ions and cyclohexane can be ruled out since, if this were the case, one would expect a higher probability for this process in the 11.7-eV photoionization (higher degree of internal excitation). As just mentioned, the opposite is true; i.e., only 30% of the $C_5H_{10}^+$ ions actually charge exchange at this energy.

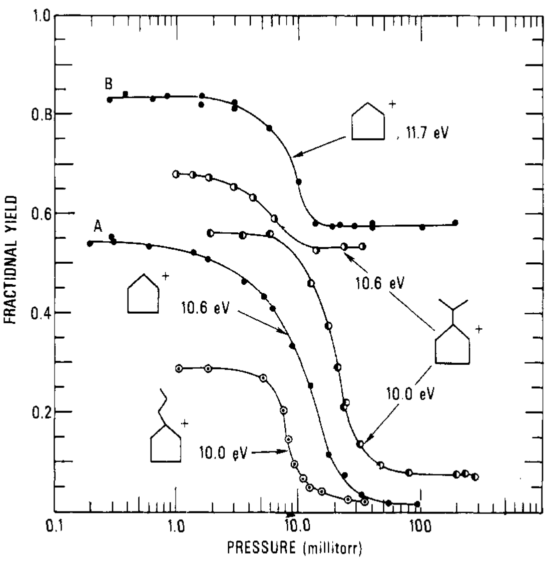

Figure 1. Fractional yields (see text for description) vs. total reaction chamber pressure. (A) Cyclopentane-cyclohexane (30:1), 10.6 eV; (B) cyclopentane-cyclohexane (10:1), 11.7 eV; (⊙) *n*-propylcyclopentane-*n*-propylcyclohexane (30:1), 10.0 eV, fractional yield/2 for clarity; (◑ and ◐) isopropylcyclopentane-isopropylcyclohexane (10:1), 10.6 and 10.0 eV, pressure scale shifted ×3 for clarity in 10.0-eV photoionization.

Four additional sets of measurements were performed at 10.62 eV. The effect of temperature on the extent of ring opening in cyclopentane was investigated in cyclopentane-cyclohexane mixtures. The results may be summarized as follows: (a) 292 K, >96% cyclic; 347 K, $\geq$94% cyclic; 386 K, 84 ± 4% cyclic; and 412 K, 78 ± 6% cyclic. (b) The equilibrium constant for the reaction $n\text{-}C_4H_{10}^+ + c\text{-}C_5H_{10} \leftrightarrow C_5H_{10}^+ + n\text{-}C_4H_{10}$ was determined from 292 to 348 K (increased decyclization precluded quantitative measurements above 348 K). A van't Hoff plot gives $\Delta H = -0.3$ kcal/mol, $\Delta S = +4.4$ eu, and $\Delta G_{300} = -1.6$ kcal/mol for the reaction as written.[10] With the IP of $n\text{-}C_4H_{10}$ as 10.50 eV,[8] a value of 10.49 eV is obtained for the IP of cyclopentane, in excellent agreement with the recommended value of 10.50 eV[8] obtained by photoionization/photoelectron spectroscopy. The addition of small quantities of cyclohexane as a charge acceptor to $n\text{-}C_4H_{10}$-cyclopentane mixtures removed $\geq$98% of the $C_5H_{10}^+$

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[10] A manuscript dealing with equilibrium measurements in a variety of alkanes and cycloalkanes will be submitted for publication shortly.

ions (as well as $C_4H_{10}^+$) at elevated pressures, verifying that the $C_5H_{10}^+$ ions produced in the equilibrium reaction retain the cyclic configuration over the temperature range studied. (c) The equilibrium constant for the reaction c-$C_5D_{10}^+$ + c-C_5H_{10} $\leftrightarrow$ c-$C_5H_{10}^+$ + c-C_5D_{10} was determined at 292 K. The value of 3.2 compares with the value of 4.0 for the analogous equilibrium in the c-C_6D_{12}–c-C_6H_{12} system.[10] (d) The reaction of c-$C_5H_{10}^+$ with NH_3 was also investigated. In contrast with cyclopropane ions, which yield only $CH_2NH_2^+$ and $CH_2NH_3^+$ as the reaction products,[6,11] only 5% of the c-$C_5H_{10}^+$ ions undergo the reaction; c-$C_5H_{10}^+$ + NH_3 $\rightarrow$ $CH_2NH_2^+$ + C_4H_9 ($\Delta H = -25 \pm 5$ kcal/mol). The major channel (95%) observed was the highly exothermic proton transfer reaction; c-$C_5H_{10}^+$ + NH_3 $\rightarrow$ NH_4^+ + C_5H_9 ($\Delta H = -45 \pm 5$ kcal/mol).

The extent of cyclic retention was also studied in several alkylcyclopentanes (see Figure 1). The results are as follows: methylcyclopentane, ≥90% cyclic, 10.0 + 10.6 eV photons; isopropylcyclopentane, 21% cyclic, 10.6-eV photons and 87% cyclic, 10.0-eV photons; and *n*-propylcyclopentane, ≥91% cyclic, 10.0-eV photons.

It is evident from the past as well as the present results that the degree of decyclization in cyclopentane and alkylcyclopentane ions depends critically upon both the initial internal energy distributions (the method of preparation in mass spectrometric studies) and the time between stabilizing collisions (radiolysis studies carried out at higher densities show that the cyclic structure is retained[4,5]).

On the basis of the data of Figure 1, which indicate that charge exchange becomes effective above 5 mtorr, a lower limit for the lifetime of c-$C_5H_{10}^+$ (10.6-eV photoionization) of approximately 10 μs may be estimated, based on the collision frequency at this pressure and assuming every collision results in stabilization.

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Deuterium Isotope Effect on the Carbon-13 NMR Spectrum of the Bicyclo[2.2.1]heptyl Cation. Nonclassical Norbornyl Cation

Sir:

The norbornyl system is at the center of the "nonclassical ion problem". Both the explanation of the solvolysis kinetics and the structure of the stable norbornyl cation have long been at issue. The argument over the stable cation concerns whether it is a rapidly equilibrating pair of classical ions or rather a symmetric (nonclassical) species. We have recently reported a new method for attacking such problems.[1-4] We now report its application to the problem of the structure of norbornyl cation.

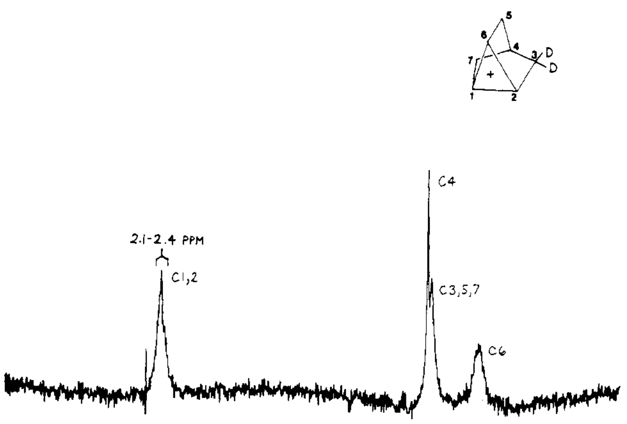
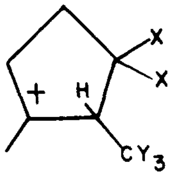


Figure 1. 67.9-MHz ^{13}C NMR spectrum of VIII at about −150 °C.

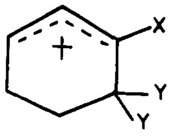
Table I. Isotopic Splitting of the C1,2 Peak in Methylene-Deuterated Analogues of the Norbornyl Cation

cation	temp, °C	isotopic splitting, ppm
I	−130	105.3[1]
IX	−110	23.9[3]
VIII	−150	<2.3

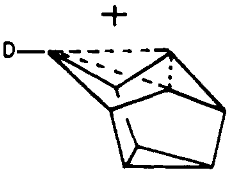
A rapid degenerate rearrangement confers functional symmetry on a carbonium ion, causing averaging of the ^{13}C NMR resonances of carbons which are interchanged by the rearrangement. Deuterium substitution perturbs this symmetry, and thereby induces large splittings in the averaged resonances.[1] The absence of a large splitting is diagnostic for a static structure.[2] Thus, in the ^{13}C NMR spectrum of the dimethylcyclopentyl ion I, the peaks for C1 and C2, which are averaged in the undeuterated ion, are split by 105 ppm at −130 °C,[1] and for II by 82 ppm at −142 °C,[1] whereas for the cyclohexenyl cations III and IV peaks for C1 and C3 are split by 0.33[2] and 0.83[4] ppm, respectively. Similarly, in the 67.9-MHz ^{13}C NMR spectrum of the [9-^{2}H]9-pentacyclo$[4.3.0.^{2,4}0^{5,7}]$nonyl cation V, the peak corresponding to C6,7,9 is shifted by less than 0.1 ppm, confirming the accepted static, symmetrical structure of the ion.[5] For the bicyclo[2.1.1]hexyl ion VI, a splitting of 1.18 ppm at −115 °C clearly demonstrates a static, bridged structure.[3]



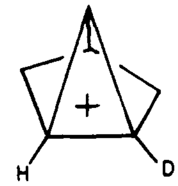
I X = D,Y = H
II X = H,Y = D



III X = D,Y = H
IV X = H,Y = D



V



VI

Both equilibrating[6a,c] and static[6b,c] structures have been proposed for the norbornyl cation. The former is an analogue of I, and its ^{13}C NMR spectrum would therefore show a large splitting of the downfield resonance upon methylene deuteration. A small splitting would argue for the nonclassical structure, by analogy with V and VI.

In the 67.9-MHz ^{13}C NMR spectrum of VIII, deuterium substituted norbornyl, prepared[7] in a mixture of SO_2ClF and

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