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Skeletal Rearrangement of the Methylcyclopentane Ion. Field-Ionization Kinetic Measurements

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Abstract: Field-ionization kinetic (FIK) measurements of the rates of loss of CH_3 and CH_4 from the molecular ion of methylcyclopentane show that at 10^{-11} to 10^{-10} sec after field ionization, the loss of CH_3 is predominant, while at 10^{-9} to 10^{-8} sec, loss of CH_4 is preferred. However, at parent-ion lifetimes $>10^{-8}$ sec, elimination of CH_3 again becomes dominant. No such reversal is observed in methylcyclohexane. These results are accounted for on the basis of two competing processes for the formation of $C_5H_9^+$ ($M - CH_3$). At short times, direct cleavage of the side chain is most important, but at longer lifetimes, opening of the five-membered ring increasingly precedes loss of CH_3. FIK measurements of methylcyclopentane-α-^{13}C reveal that at times $<10^{-9}$ sec, at least 95% of the $C_5H_9^+$ ions formed does not contain the labeled C atom. At longer times, a progressively larger fraction of the $C_5H_9^+$ ions does contain the tagged atom, approaching statistical randomization at $\sim 10^{-5}$ sec. This result confirms the hypothesis above and suggests that the ionized alkene resulting from ring opening can undergo further skeletal isomerization prior to elimination of CH_3. The $C_4H_8^+$ fragment ions formed by loss of C_2H_4 from the labeled molecular ion were found to contain the labeled side chain to an extent >95% at 10^{-10} to 10^{-11} sec, but only 75% at 10^{-5} to 10^{-6} sec. It is suggested that there is a rapid, specific pathway for elimination of C_2H_4 at short times, while at longer times, an ionized alkene intermediate has sufficient time to undergo intramolecular rearrangement prior to elimination of C_2H_4.

The gaseous ion chemistry of cycloalkanes presents many complexities. One of the more interesting of these arises in the mass spectra of alkyl cycloalkanes, which often (but not always) show a significant peak corresponding to the loss of the alkyl side chain from the molecular ion.[2] In 1958, Stevenson[3] showed by means of isotopic labeling experiments that when methylcyclopentane undergoes loss of a methyl radical following electron-impact (EI) ionization, about half of the original methyl carbon atoms are retained by the remaining $C_5H_9^+$ ions. Further detailed studies with both ^{13}C- and D-labeled compounds by Meyerson et al.[4,5] demonstrated that the loss of the alkyl side chain in both methyl- and ethylcyclopentane proceeds by (at least) two competing pathways. One of these pathways apparently corresponds to the expected simple bond cleavage, but a significant fraction of the molecular ions must decompose by means of an intramolecular rearrangement followed by (or in concert with) bond scission.[4,5]

The convincing evidence for the presence of competing modes of unimolecular decomposition strongly suggested to us that a kinetic study of the reactions involved would shed important new light on the details of these processes. The field-ionization kinetic (FIK) method[6,7] which has been employed in the work reported here permits the study of unimolecular decomposition reactions of (radical) ions over a range of molecular-ion lifetimes extending from 10^{-11} to 10^{-5} sec. Molecular ions produced by field ionization have relatively low internal energies[8] as compared with the molecular ions formed by standard electron-impact (EI) techniques. The resulting reduction in the number of available competing decomposition-reaction channels can greatly simplify the interpretation of the results in terms of gas-phase reaction mechanisms. The results of previous FIK studies[9,10] have shown that these data can offer a more detailed and complementary view of essentially the same gas-phase unimolecular decomposition phenomena which are observed following other ionization processes, particularly those which impart a relatively low energy to the molecular ion.

Experimental Section

The experimental results reported here were obtained with a modified double-focusing mass spectrometer of Mattauch–Herzog geometry[11] (Du Pont/CEC 21-110B) equipped with a modified[7] combination FI–EI ion source and an electrical detection system. Commercial uncoated stainless steel razor blades were used as FI emitters. Curves of ion current vs. blade voltage were recorded on an X-Y recorder, by setting the magnetic analyzer for a particular fragment ion and varying blade voltage in increments of 10 V.

Detailed descriptions of the FIK technique employed here[7] and the theory behind it[6,7] have been published, as have the details of the calculations required to convert the curves of ion current vs. blade voltage to curves of reaction rate as a function of time.[7,12] In brief, ions formed at or very near the emitter edge (either by ionization or fragmentation) are fully accelerated when leaving the source and have the correct amount of translational energy to be transmitted by the electric sector analyzer (ESA); they are then momentum analyzed by the magnetic sector and detected in the usual fashion. These ions constitute the "normal FI spectrum". Fragment ions formed by gas-phase unimolecular decompositions occurring at some distance from the emitter are energy deficient and are therefore rejected by the ESA. These ions can, however, be

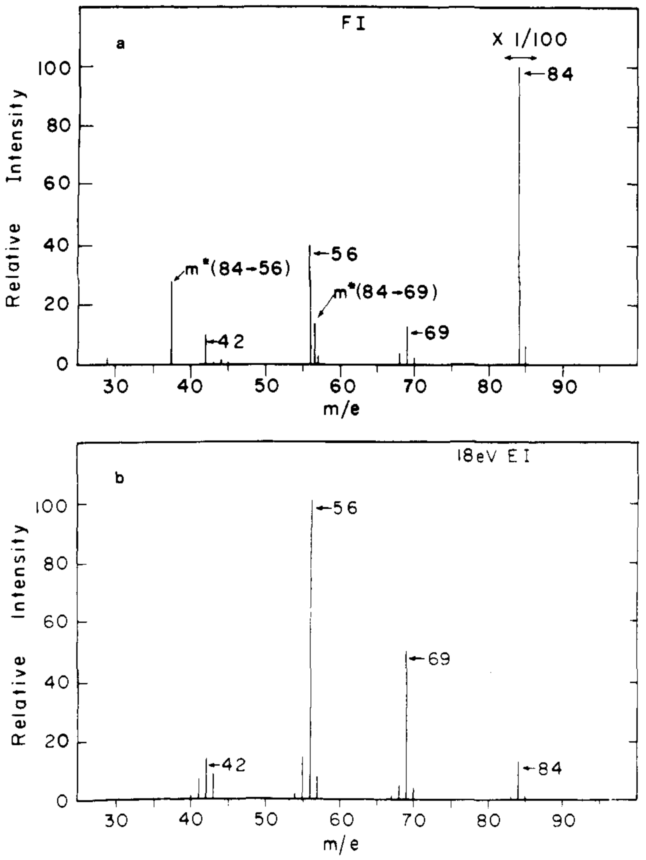


Figure 1. (a) Double-focusing FI mass spectrum of methylcyclopentane. A very weak metastable peak for the transition 84 → 68 was also observed in this spectrum. (b) Electron impact (18 eV nominal) mass spectrum of methylcyclopentane.

detected by increasing the emitter voltage sufficiently so that they will pass through the ESA. A curve of ion current (number of ions transmitted) vs. emitter voltage is therefore a measure of the number of decompositions occurring at various distances from the emitter. A knowledge of the parent-ion trajectory[12,13] enables one to convert these distances to corresponding parent-ion lifetimes so that a curve of rate of formation of a particular fragment ion as a function of parent-ion lifetime is finally obtained.

Fragment ions resulting from decompositions in the small volume between the two halves of the focusing slit lens produce a peak in the ion current vs. blade voltage curve[7] at a blade voltage approximately equal to:[14]

$$V = (M/m)V_0 - [(M/m) - 1]V_F$$

where V_0 is the normal instrument accelerating voltage, V_F is the voltage at the focus slit, and M and m are the parent- and fragment-ion masses, respectively. The relative rates of competing decomposition reactions in this region were determined by comparing the peak intensities due to each reaction. In order to measure the peak heights, it was necessary to extrapolate the ion current vs. blade voltage curves from lower blade voltages to the voltage at which the focus peak occurred. This extrapolation provided the base line from which the peak heights were measured.[7]

Intensities of unimolecular decompositions occurring in the field-free region of the mass spectrometer between the source and the ESA were measured by reducing the ESA voltage[15] and adjusting the magnet to mass $m^* = m^2/M$. Decompositions in the second field-free region (between the ESA and the magnet) appeared as metastable peaks in the normal FI mass spectrum.

All FI data reported here were taken at a source temperature of 50°.

The low-energy (18 eV nominal) EI specturm of methylcyclopentane was obtained on a Varian-MAT 311 mass spectrometer coupled to an XDS Sigma 2 computer.[16] Source temperature was 200°.

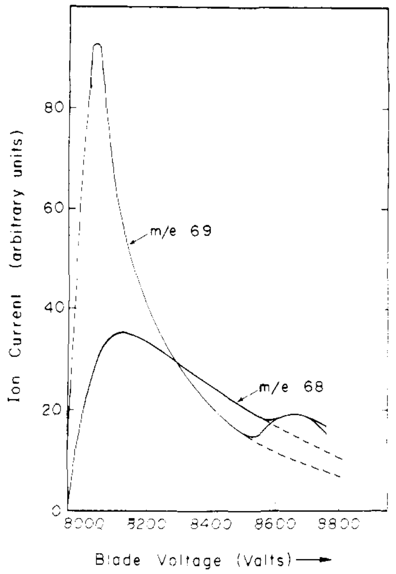


Figure 2. Curves of ion current vs. blade voltage for fragment ions of *m/e* 68 and 69 from methylcyclopentane. The dashed portions of the curves are extrapolations used to calculate the rates of decomposition at the focusing electrodes.

Labeled methylcyclopentane-α-^{13}C was prepared according to the method described by Stevenson[3] and isolated and purified by gas chromatography. Its isotopic purity, determined by high- and low-energy EI and FI mass spectrometry, was 81%. Unlabeled methylcyclopentane and methylcyclohexane were obtained from Aldrich, and their purities were checked by gas chromatography and mass spectrometry.

Results

Methylcyclopentane. The FI mass spectrum of methylcyclopentane (MCP) is shown in Figure 1a. Figure 1b contains the 18-eV (nominal) EI mass spectrum of this compound for comparison. The FI spectrum contains strong metastable peaks and a very large molecular-ion intensity, but the two spectra have important similarities. Fragment ions resulting from loss of C_2H_4 (to give *m/e* 56) and CH_3 (*m/e* 69) from the molecular ion give the most important fragment-ion peaks with loss of C_3H_6 (*m/e* 42) occurring to a lesser extent. But these spectra do not tell the whole story. The loss of CH_4 from the molecular ion to give *m/e* 68 produces a relatively minor peak in both spectra, but the curves of fragment-ion current for *m/e* 68 and 69 as a function of blade voltage (Figure 2) reveal that at some parent-ion lifetimes following FI, the rate of formation of *m/e* 68 in fact exceeds the rate of formation of *m/e* 69. In this figure, higher blade voltages correspond to longer parent-ion lifetimes, and the ion current for each ion is proportional to the rate of formation of that ion.[7] Since both fragment ions come from the same parent ion, and their masses differ only slightly, the ratio of their rates of formation is essentially equal to the ratio of the fragment-ion currents at any given time.[7] The structure in the curves above ~8500 V is due to decompositions at the focusing lens (vide supra). All voltages have been corrected for the small voltage drop at the blade surface.[7,17]

The course of the competition between these two modes of fragmentation over the entire accessible time range is illustrated in Figure 3. The figure is a plot of the ratio of the phenomenological rate constants[7] $\bar{k}(t)$ for the two processes as a function of time. A log-log format was used for convenience in presentation of data spanning several orders of magnitude. The overall rates of both reactions decrease continuously with time after ~10^{-10} sec, although their

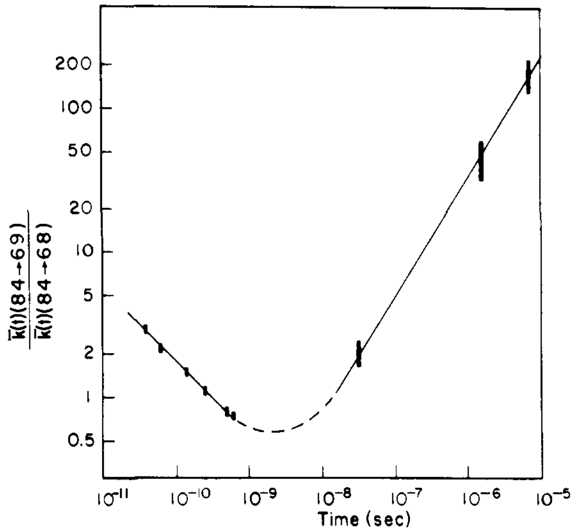


Figure 3. Ratio of the phenomenological rate constants $\bar{k}(t)$ for formation of ions of *m/e* 68 and 69 from methylcyclopentane as a function of parent-ion lifetime.

Table I. Relative Rates of Formation of $(M - CH_3)^+$ and $(M - CH_4)\cdot^+$ Ions at Various Times Following Field Ionization of Methylcyclohexane

Time, sec	$(M - CH_3)^+/(M - CH_4)\cdot^+$
5×10^{-11}	13
1×10^{-9}	6.6
3×10^{-8}	3.9
1×10^{-5}	1.7

Table II. Relative Amounts of *m/e* 68, 69, and 70 Ions Formed from Methylcyclopentane and Methylcyclopentane-α-^{13}C at Various Times Following FI

	Methylcyclopentane-α-^{13}C *m/e*			Methylcyclopentane *m/e*	
Time, sec	68, %	69, %	70, %	68, %	69, %
4×10^{-11}	25 ± 5	75 ± 5	~0	26	74
1.5×10^{-10}	43	57	~0	40	60
7×10^{-10}	58	42	~0	57	43
3×10^{-8}	36 ± 10	24 ± 10	40 ± 10	33	67
1.5×10^{-6}	1 ± 0.3	22 ± 5	76 ± 5	2	98
7×10^{-6}	<1	21 ± 3	78 ± 3	<1	>99
Calculated (total randomization)[a]	0	17	83	0	100

[a] Calculated assuming total carbon randomization and no loss of CH_4.

ratio does not. The points on the graph at times shorter than 10^{-9} sec were calculated from data taken from the continuous curves in Figure 2. The point at 3×10^{-8} sec represents the focus-region data, also obtained from Figure 2, and the two points at longer times are intensity ratios measured in the first and second field-free regions of the mass spectrometer. The length of the vertical bars represents the estimated maximum uncertainty in each measured ratio. The exact shape of the dashed portion of the curve is not determined by the data. The curve shown represents the sum of the two (extrapolated) straight segments. All data were corrected for naturally occurring ^{13}C.

Two additional gas-phase reactions were detected: namely, loss of C_2H_4 and C_3H_6 from the molecular ion. The intensity of the *m/e* 56 ion $(M - C_2H_4)$ was approximately equal to the sum of the *m/e* 68 and 69 intensities over the time range 10^{-11} to 10^{-9} sec. At times longer than $\sim 3 \times 10^{-8}$ sec, its intensity was about three times their sum. The *m/e* 42 intensity was about one-fourth of the *m/e* 56 intensity from 10^{-11} to 10^{-9} sec and was not detectable at any time longer than $\sim 10^{-8}$ sec.

Methylcyclohexane. The FI mass spectrum of methylcyclohexane (MCH) shows the presence of two relatively strong metastable peaks corresponding to the loss of CH_3 and CH_4 from the molecular ion. The results of the FIK measurements for these two transitions are summarized in Table I. In marked contrast to the methylcyclopentane results, the ratio of $(M - CH_3)^+$ to $(M - CH_4)\cdot^+$ clearly decreases continuously with time over the entire accessible time range.

Some minor formation of *m/e* 70 fragment ions (loss of C_2H_4 from the molecular ion) was also observed. The intensity of *m/e* 70 formed in the gas phase was less than 1% of the $(M - CH_3)^+$ intensity at all times shorter than $\sim 10^{-7}$ sec but was about 8% of the $(M - CH_3)^+$ intensity in the second field-free region ($\sim 10^{-5}$ sec).

Methylcyclopentane-α-^{13}C. In order to examine more carefully the atoms involved in the presumed rearrangements of MCP, a sample of methylcyclopentane-α-^{13}C (MCP-α-^{13}C) was prepared and studied in the same manner as the unlabeled material. The results are summarized in Table II. The first three columns of the table give the relative amounts of *m/e* 68, 69, and 70 fragment ions formed (as percentages of the total current for all three ions) at various times following ionization. The data at times $<10^{-9}$ sec were obtained from the accelerating voltage scans for each ion (cf. Figure 2). The data for 3×10^{-8} sec represent the focus region, and the remaining two measurements are from the two field-free regions. The results have been corrected for the presence of unlabeled methylcyclopentane and for naturally occurring ^{13}C, assuming no isotope effects.

It is clear that all of the *m/e* 68 ions formed from the labeled compound must be due to the loss of $^{13}CH_4$, and that all of the *m/e* 70 ions (after correction for natural ^{13}C) are due to loss of unlabeled CH_3 from the molecular ion.[18] The *m/e* 69 fragment ions could, of course, be formed either by loss of $^{13}CH_3$ or CH_4. However, by comparing these results with those for the unlabeled material (columns 4 and 5 of Table II), it is seen that at times less than $\sim 10^{-9}$ sec, the proportions of *m/e* 68 and 69 ions are the same for both the labeled and unlabeled compound within the limits of accuracy of the data. At the longer times, the relative amounts of *m/e* 68 ions formed are also not significantly different (columns 1 and 4), and the sum of *m/e* 69 and 70 ions from the methylcyclopentane-α-^{13}C is approximately equal to *m/e* 69 ions from the unlabeled material. Thus, in the absence of large isotope effects,[19] no significant fraction of the *m/e* 69 ion current from MCP-α-^{13}C can be due to $M - CH_4$. This indicates that at shorter times ($<10^{-7}$ sec), most or all of the methane lost from the molecular ion contain the carbon atom and presumably the three attached hydrogen atoms which composed the original side chain. At times $>10^{-6}$ sec, the amount of methane lost is so small that it is not possible to determine the origin of the carbon atom in the neutral CH_4 fragment. The maximum possible contribution of $M - CH_4$ to the *m/e* 69 ion intensity (that is, assuming complete randomization prior to loss of CH_4) is five times the *m/e* 68 ion intensity.

The virtual absence of *m/e* 70 ions at times $<10^{-9}$ sec shows that at least 95% of the methyl radicals lost from the molecular ion within 10^{-9} sec contains the original alkyl side-chain carbon atom. At longer times, the situation changes drastically, closely approaching or reaching total

Table III. Relative Amounts of *m/e* 56 and 57 Fragment Ions Formed from Methylcyclopentane-α-^{13}C at Various Times Following FI

Time, sec	*m/e* 56, %	57, %
6×10^{-11}	~0	100
2×10^{-10}	3	97
7×10^{-10}	15	85
1×10^{-9}	20	80
3×10^{-8}	23 ± 5	77
2×10^{-6}	25 ± 3	75
7×10^{-6}	25 ± 2	75
Calculated (total randomization)	33	67

randomization within the limits of experimental accuracy. Thus, at short times, loss of methyl apparently occurs via a direct pathway, while at longer times, the loss of a methyl radical is largely preceded by one or more skeletal rearrangement steps.

The loss of ethylene from the molecular ion can give a fragment ion of *m/e* 56 or 57. Table III shows the relative amounts of these two fragment ions formed at various times, along with the calculated values which would be expected if total randomization occurred prior to fragmentation. The data have been corrected for the presence of unlabeled material and for naturally occurring ^{13}C, assuming no isotope effects. The results show that at the very shortest times, C_2H_4 is eliminated essentially entirely from the elements of the ring, while at longer times, progressively more ^{13}C is contained in the neutral C_2H_4 fragment, presumably indicating again the operation of intramolecular skeletal rearrangement prior to the loss of C_2H_4. Total randomization is not achieved by 7×10^{-6} sec, however, suggesting that the rearrangement processes available to the molecular ions may not be sufficient to render it equally likely that each of the carbon atoms will be incorporated in a C_2H_4 neutral fragment.

Discussion

The EI results of Stevenson[3] and Meyerson et al.[4] for methylcyclopentane-α-^{13}C are quite consistent with the FIK results presented here. Stevenson found 52% retention of the labeled atom in $C_5H_9^+$ fragments, while Meyerson reported 42% retention. The discrepancy between these two figures was later explained by Meyerson[5] on the basis of different parent-ion residence times in the ion source. The FIK results are clearly consistent with this explanation. The $^{13}CC_4H_9^+$ and $C_5H_9^+$ intensities reported in the EI studies represent the integrated intensities of fragment ions formed from the time of primary ionization up to about 2 μsec later.[20] The FIK data show that the percent of label retention in $C_5H_9^+$ ions formed within this time period ranges from >95 to ~22%, and that it is a strong function of reaction time. Similarly, the reported[3,4] 80% label retention in $C_4H_8^+$ ions ($M - C_2H_4$) produced by EI is quite consistent with the data presented in Table III. The suggestion of Meyerson et al.[4,5] that more than one process contributes to the formation of $C_5H_9^+$ is thus supported, and if the analogy between EI and FI induced processes is valid, it seems evident that $C_4H_8^+$ fragment ions may be formed in more than one way as well.

Possibly the most significant feature of the FIK results, however, is the reversal of the trend in Figure 2 toward increasing dominance of the decomposition leading to loss of the elements of methane:

$$M^+ \longrightarrow (M - 16)\cdot^+ + CH_4 \qquad (1)$$

over the reaction resulting in the loss of methyl:

$$M^+ \longrightarrow (M - 15)^+ + \cdot CH_3 \qquad (2)$$

Consider first the situation at times $<10^{-9}$ sec. The observed behavior of the methylcyclopentane molecular ion at short times is what would be expected on the basis of the quasi-equilibrium theory (QET)[21] for a competition between a high frequency-factor (ν), high activation-energy (E_0) fragmentation and one with relatively low ν and E_0.[22,23] Those parent ions with a greater amount of internal energy will decompose at shorter times on the average and will tend to prefer the decomposition pathway with the highest frequency factor, assuming that they have more than the required activation energy for either path. At slightly longer times, the average internal energy of the decomposing ions will be smaller. An increasing fraction of them will not possess enough internal energy to decompose via the higher activation-energy process and will be forced to take the lower frequency-factor pathway. The number of ions decomposing via the low frequency-factor, low-activation energy path will therefore undergo a relative increase as time goes on. This situation can be described in terms of a crossing of the k (microscopic rate constant) vs. E (internal energy) curves for the two competing reactions[22-24] and commonly occurs when a simple cleavage reaction (high ν, high E_0) is in competition with a rearrangement (low ν, low E_0) reaction.[22-24]

Reactions 1 and 2 in methylcyclopentane at times less than ~10^{-9} sec appear to fit this description. An indication of the relative activation energies of reactions 1 and 2 can be obtained from appearance potential measurements for several isomeric C_6 (ref 25), C_5, and C_4 (ref 26) alkanes. In each case, the appearance potential for $(M - CH_3)^+$ is 0.1-0.5 eV higher than that for $(M - CH_4)\cdot^+$, implying that the activation energy for the formation of the latter ion is indeed smaller than that for the former. In addition, the data of Meyerson et al.[4] on unlabeled methylcyclopentane show about a 50% enhancement of the $(M - CH_4)\cdot^+$ peak with respect to the $(M - CH_3)^+$ peak as the ionizing voltage was reduced from 15 to 8 eV (nominal).

Comparison of the short time methylcyclopentane results with those for methylcyclohexane adds further evidence that the observed behavior is a simple cleavage/rearrangement competition. The relative importance of reaction 1 in methylcyclohexane increases continuously with increasing parent-ion lifetime for all accessible times (Table I) as would be predicted on the basis of the QET model described above. It is assumed here that the $C_6H_{11}^+$ ion formed in reaction 2 is an unrearranged cyclohexyl ion. That this is very likely true, at least following EI ionization, is demonstrated by the results of Meyerson et al.[4] that the loss of methyl radical from methylcyclohexane involves only the original side chain and by several appearance potential measurements.[27] A similar competition between reactions 1 and 2 was found in an FIK study of 2-methylpropane.[28,29] As with methylcyclohexane, the importance of reaction 2 with respect to reaction 1 was found to decrease continuously with increasing time.

It should be noted that the specific loss of a labeled methyl radical from MCP-α-^{13}C at short times does not necessarily prove that the five-membered ring remains intact. However, the combination of these labeling data with the fact that the behavior of methylcyclopentane at times $<10^{-9}$ sec parallels that of methylcyclohexane and 2-methylpropane certainly gives very strong support to this hypothesis. If this is in fact the case, then the *reversal* of the relative trends of reactions 1 and 2 in methylcyclopentane at ~10^{-8} to 10^{-9} sec (cf. Figure 3) strongly suggests that a structural reorganization, presumably ring opening (vide infra), has begun to come into play at these longer times.

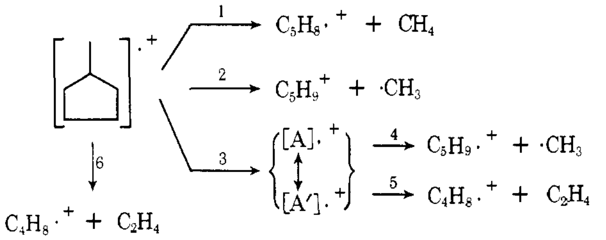
The change in the pattern of the two reactions can only be due to a change in their relative frequency factors and/or activation energies, provided that no excited electronic states are involved.[30] Although the presence of such excited states cannot be completely excluded, their participation seems improbable since the average internal energy of field-ionized molecules is known to be small.[8]

It has been argued with some success that the relative abundances of fragment ions stemming from slow decompositions of metastable ions produced by EI ionization of various molecules can be used to ascertain their identity.[31,32] Care must be exercised to take account of possible differences in internal-energy distributions of different parent ions, however.[33] In the work described here, the measurement of the relative abundances of two major fragment ions of methylcyclopentane is somewhat analogous to the EI studies,[31,32] but with the very important additional advantage of the ability to observe this competition as a function of time for a single parent-ion species.

There is considerable evidence to support the idea of ring opening prior to fragmentation in EI ionized cyclopentanes.[27,34-37] The available FIK data tend to indicate similar behavior following FI. FIK measurements on several isomeric C_6H_{12} monoalkenes[38] and 2-methylpropene[39] showed that the formation of $(M - 16)^+$ ions by gas-phase unimolecular decomposition of the molecular ions was very slow or undetectable in all cases studied, whereas the loss of methyl was an important reaction in these molecules at all parent-ion lifetimes from 10^{-11} to 10^{-5} sec. The fact that the behavior of methylcyclopentane at long parent-ion lifetimes is much more typical of that of an unsaturated ion than a saturated one clearly suggests a structural similarity with the former.

The results described above can be rationalized in terms of Scheme I which shows the postulated main gas-phase unimolecular decomposition pathways of methylcyclopentane. The $C_5H_9^+$ and $C_5H_8\cdot^+$ ions which are formed from methylcyclopentane-α-^{13}C at times less than $\sim 10^{-9}$ sec contain essentially none of the labeled carbon atoms. Reactions 1 and 2, which are presumed to be most important at these short times, occur directly from the unrearranged molecular ion and are therefore isotopically specific. Reaction 1 is the only process shown by which $C_5H_8\cdot^+$ ions can be formed. Thus if the scheme is correct, the presence of this ion is indicative of the presence of unrearranged molecular ions containing enough internal energy to decompose via this path. Meyerson et al.[4] in fact observed no internal skeletal or hydrogen rearrangement prior to the loss of CH_4 from labeled methylcyclopentanes, in agreement with Scheme I and the FIK results. Loss of a methyl radical can occur either directly via reaction 2 or from the intermediate A (or A′). It is assumed that the cyclopentane ring has opened in these intermediates so that they have the structure of an ionized alkene. (Reaction 3 + 4 could also lead to specific loss of the original methyl side chain. This could occur for instance, if the unrearranged parent ion were to undergo ring opening to 1-hexene[3] in which the original side chain became the terminal methyl group, which could then be eliminated.) In order to explain the observed isotopic composition of the fragment ions at longer times, it is necessary to postulate one or more further skeletal rearrangements of the intermediate A, leading to isomer(s) A′. Convincing evidence that structural isomerization of alkene ions is possible has been presented. Ausloos et al.[40,41] showed that 1-$C_4H_8^+$ ions isomerize readily to 2-$C_4H_8^+$ and *i*-$C_4H_8^+$ ions when formed with an initial energy of 11.6–11.8 eV, although not when the initial 1-$C_4H_8^+$ energy was 10 eV. Meisels et al.[42] demonstrated carbon skeletal rearrangement resulting in complete loss of carbon identity in butene ions following low-energy EI by means of ^{13}C labeling. There are several other examples in the literature as well.[34,43-46] The question of whether the low-energy ions produced by FI have enough internal energy to induce such isomerization is not directly answered in these studies. However, an examination of the heats of formation of the molecular ions of methylcyclopentane and several isomeric alkenes[25] shows that the latter are between 0.8 and 2.0 eV more stable than the former. In the absence of deactivation by collision or radiation, this energy must appear as additional internal energy in an alkene ion formed by ring opening and could well be sufficient to induce subsequent skeletal isomerization.

Scheme I



Considerable amounts of $C_4H_8\cdot^+$ ions are formed at very short times ($<10^{-10}$ sec) from methylcyclopentane following FI, yet the isotopic specificity of both these ions and the $C_5H_9^+$ ions formed at these times shows that little isomerization of the molecular ion can have occurred. There must, therefore, be a specific path for formation of $C_4H_8\cdot^+$ from the parent ions at short times which results in the loss of two of the original ring carbons. A similar process is probably implicated following EI ionization in view of the result[4] that in this case, most of the C_2H_4 eliminated from MCP and virtually all of that from ethylcyclopentane come from the elements of the ring. These data may indicate the presence of a specific rapid reaction operating in parallel to reaction 3 + 5 at short times. Reaction 6 in Scheme I represents this possibility.

It is not necessary, however, to propose a separate reaction pathway parallel to reaction 3 + 5 in order to explain these results, although the existence of such a path is certainly not ruled out by our results. Consider the following scenario. Assume that reaction 4 has both a lower frequency factor and a lower activation energy than reaction 5. Assume further that a significant amount of the intermediate $A\cdot^+$ is formed in a specific way at very short times, and that it cannot rearrange to a detectable degree in less than $\sim 10^{-10}$ sec. Then at short times, most of the reactive $A\cdot^+$ could decompose by reaction 5 in a specific fashion, while only a small amount of $C_5H_9^+$ would be formed (via reaction 4) in comparison to the amount formed in reaction 2. At longer times, three changes will have occurred: (1) $A\cdot^+$ will have isomerized to some degree; (2) the average internal energy of the decomposing ions will have decreased so that reaction 4 will be able to compete more successfully with reaction 5; and (3) the concentration of reactive parent ions with the intact ring structure will have decreased relative to that of reactive A^+ ions, thereby suppressing reaction 2. Therefore, both the $C_5H_9^+$ and $C_4H_8\cdot^+$ ions formed at longer times will evidence some intramolecular skeletal isomerization of their parent ions. This mechanism is, of course, only speculative, but it is at least consistent with the datum[38] that 1-hexene loses C_2H_4 more rapidly than CH_3 at short times following FI, but more slowly at long times.

The details of the process by which C_2H_4 is eliminated from field-ionized methylcyclopentane are not known. It has been noted that the loss of C_2H_4 from the straight-chain 1-pentene ion following EI occurs predominantly by the loss of the end of the molecule containing the double bond.[36] If this were the loss mechanism for a 1-hexene intermediate in the FI case, it could account for the short-time results. On the other hand, Kraft and Spiteller[47] reported that a six-center McLafferty type rearrangement provides the major pathway for C_2H_4 loss in many branched alkenes. Again, in the FI case, an intermediate with either the 2-methyl-1-pentene or 3-methyl-1-pentene structure could produce the observed results. The case for this latter mechanism is strengthened by the results of Smith and Williams,[34] who studied metastable decompositions from a number of C_6H_{12} isomers, including methylcyclopentane, and concluded that for all of the isomers studied, ethylene loss occurred from the 2-methyl-1-pentene structure, whereas methyl loss occurred from the 2-methyl-2-pentene ion. These two structures differ only by a 1,3 allylic hydrogen rearrangement, a process which is thought to be very rapid following FI.[10,39] Further suggestive evidence for a six-center rearrangement as the most probable pathway for C_2H_4 loss is the fact that this type of reaction, in esters[9] and ketones[48] as well as alkenes,[38,47] is known to be very important following FI and low-energy EI. Further FIK studies are currently underway with a view to exploring these various possibilities and, it is hoped, to more specifically identifying the structures involved.

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