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Ring Opening Reactions in Cycloalkane Molecular Ions. A Collisional Activation and Field Ionization Kinetic Study[1]

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Abstract: Collisional activation and field ionization kinetic measurements demonstrate that alkyl substituted cycloalkane molecular ions with three-, four-, and five-membered rings (*n*-pentylcyclopropane, *n*-butylcyclobutane, 1,2-diethylcyclobutane, and *n*-propylcyclopentane) undergo ring opening within ca. 10^{-9} s to form initially the 1-alkene molecular ions which isomerize to some extent to double bond isomers. However, six-, seven-, and eight-membered rings (ethylcyclohexane, 1,2-dimethylcyclohexane, 1,3-dimethylcyclohexane, methylcycloheptane, and cyclooctane) remain intact *prior* to decomposition.

The occurrence of ring-opening reactions in alkylcycloalkane molecular ions prior to fragmentation has been postulated repeatedly. Thus, Stevenson[3] demonstrated that if methylcyclopentane-α-^{13}C undergoes loss of a methyl radical about 50% of the label is retained in the remaining $[C_5H_9]^+$ ion suggesting an isomerization to a linear ion prior to decomposition. More detailed studies by Meyerson et al.[4,5] using compounds labeled with ^2H and ^{13}C in the α position showed that the label retention in the $[C_5H_9]^+$ ion is nearer to 40% and depends on the ionizing voltage; with increasing electron energy the loss of the original side chain becomes more pronounced. From these results the authors concluded that at least two competing mechanisms are operating, i.e., loss of the original side chain from the intact ring and methyl loss after ring opening to a linear intermediate. Similar results were obtained for ethylcyclopentane,[4] although a shift toward simple cleavage has been postulated with increasing length of the side chain. In contrast to these alkylcyclopentane ions the methyl radical lost from methylcyclohexane includes only the original side chain.[4]

An extensive and elegant field ionization kinetic study by Falick and Burlingame[6] fully supported the earlier conclusions and shed further light on the details of these processes. The lifetime measurements of methylcyclopentane-α-^{13}C revealed that at times $<10^{-9}$ s exclusively the side chain is eliminated while the methyl radical loss at longer times included also ring C atoms approaching total randomization at the longest observed times suggesting that the ring is essentially intact at times $<10^{-9}$ s prior to decomposition, but opens up at longer times.

A completely different approach was used by Pottie et al.[7] to obtain information on the structure of cycloalkane ions. From heats of formation data obtained from appearance potential measurements the authors concluded that there is a "strong possibility" that the $[C_nH_{2n-1}]^+$ ions formed from cyclopropane, cyclobutane, and methylcyclopentane have an olefinic rather than a cyclic structure, while the $[C_6H_{11}]^+$ ion from cyclohexane actually may be a cyclohexyl ion.

In this context also a study of the isomerization of $[C_6H_{12}]^{+\cdot}$ ions by Smith and Williams is of interest.[8] Using competing metastable transitions the authors concluded that the decompositions of a large variety of $[C_6H_{12}]^{+\cdot}$ ions proceed via common intermediates. Although in view of the presented data this conclusion is not fully convincing,[9] rather similar metastable abundance ratios were observed for *n*-propylcyclopropane, ethylcyclobutane, and methylcyclopentane.

Finally, in a collisional activation (CA) study[10] of a large number of C_8H_{16} isomers (including some cycloalkanes) identical CA spectra were observed for the molecular ions of 1-octene and *n*-propylcyclopentane which again strongly suggests ring opening of the latter prior to decomposition.

Stimulated by this observation we decided to study a whole series of isomeric cycloalkanes of the elemental composition C_8H_{16} with three-, four-, five-, six-, seven-, and eight-membered rings and varying side chain using both the collisional activation[11] and field ionization kinetic[12] technique to obtain additional information on the following questions: (a) the dependence of the stability of the cycloalkane molecular ion on the ring size, (b) the influence of the length of the side chain on the isomerization behavior, (c) the structure of the molecular ion after ring opening, and (d) the time scale for the isomerization process.

Experimental Section

Materials. Methylcycloheptane. Reaction of cycloheptanone with CH_3MgBr gave 1-methylcycloheptanol, which was thermally dehydrated to 1-methylcycloheptene under addition of I_2.[13] Catalytic hydrogenation ($H_2/PtO_2/AcOH$) led to methylcycloheptane.

***n*-Butylcyclobutane.** Cyclobutanone was transformed into the corresponding alcohol with *n*-C_4H_9Li which was dehydrated (I_2 ad-

dition)[13] to 1-(*n*-butyl)cyclobutene-(1) and butenylidenecyclobutane. Catalytic hydrogenation of the two olefines ($H_2/PtO_2/Et_2O/AcOH$) led to *n*-butylcyclobutane.

***n*-Pentylcyclopropane.** Heptene-(1) was transformed into 1,1-dibromo-2-(*n*-pentyl)cyclopropane using phase-transfer catalysis[14] with $CHBr_3/NaOH/TEBA$. The bromine was removed by reduction with $LiAlH_4$[15] (40 h reflux in an etheric suspension). All compounds were purified by GC and the constitutions verified by H NMR, IR, and MS. All other compounds were purchased from Fluka and used without further purification.

Instrumental Details. Collisional activation spectra were obtained with a self-constructed double-focusing mass spectrometer of reversed geometry (magnetic sector field preceding electrostatic sector field) equipped with a collision cell in front of the energy resolving slit (acceleration voltage, 8 kV; electron energy, 70 eV, if not stated otherwise; electron beam, 20 μA; source temperature, ca. 150 °C). Samples were introduced via the gas inlet system kept at room temperature. Collisional activation spectra were taken using the following procedure: The magnetic and electrostatic sector fields were adjusted to pass $[C_8H_{16}]^{+\cdot}$ ions. The target gas (helium) was then introduced into the collision cell via a variable leak valve and the leak rate increased until the precursor ion intensity decreased to $\frac{1}{3}$ of its original value due to scattering and decomposition ($\sim 5 \times 10^{-5}$ Torr). CA spectra were obtained by scanning the electrostatic sector potential, recorded on an XY recorder and normalized to the sum of all fragments. Only peak heights were measured and the abundance not corrected for reduced multiplier response. The CA spectra were independent of the electron energy within the reproducibility. Thus, no corrections for contributions from metastable decompositions which may be energy dependent were carried out. All CA spectra are the means of two measurements. The long time reproducibility was checked with 1-octene measured at the beginning and the end of the series and was better than ±5%.

An instrument of identical geometry, but equipped with a nonfocussing field ionization source, was used for ion lifetime measurements. A potential of +7 kV was applied to the emitter, a tungsten wire of 8 μm diameter briefly activated with benzonitrile.[16] The slotted counterelectrode, at a potential of −2 kV was placed 2 mm below the emitter. The original lense system of the ion source was replaced by two retardation boxes kept at ground potential during normal operation of the source. Meshes of high transparency were fixed to all slits in these boxes to reduce their focussing properties. The decay between the emitter and the counterelectrode ($\sim 10^{-11}$–2×10^{-8} s) was determined by adjusting the electrostatic analyzer potential to transmit the molecular ion, increasing the acceleration voltage stepwise and scanning the magnet each time over the mass range of interest. Using this procedure it is possible to obtain complete mass spectra as a function of the ion lifetime. However, as the ion lifetime depends on the mass of the fragment ion[17] it also varies within one spectrum. This variation is especially pronounced at long lifetimes; e.g., at an emitter potential of 7900 kV the fragment at *m/e* 42 from 1-octene is formed after a molecular ion lifetime of 2×10^{-10} s, that of *m/e* 97 after 3×10^{-9} s. Nevertheless, the mass spectra obtained by this procedure allow a qualitative survey of the decay of the molecular ion as a function of the ion lifetime. From the individual data in each spectrum the rate of the fragment ion formation, di/dt, was calculated as function of the lifetime for all major peaks as described previously[17,18] using the average of at least three measurements.

By applying a constant voltage (+2.2 kV) to the retardation boxes the decay within this region[18] (0.6–3×10^{-7} s) can be measured. The decomposition within the first (0.6–4×10^{-6} s) and the second (0.6–1×10^{-5} s) field free region was determined using the normal refocussing techniques.[19] The decomposition between emitter and counterelectrode was corrected for enhanced ionization efficiency with rising acceleration voltage and for isotopic contributions. Metastable ions were corrected for reduced multiplier response. To reduce the influence of the high electric field on the internal energy distribution of the molecular ion, all measurements were carried out with a heated emitter (~700 °C) so that the internal energy of the field ionized molecular ion consisted predominantly of the thermal energy.

Results and Discussion

Collisional Activation Spectra. CA spectra were used to obtain information on the isomerization of the cycloalkane molecular ions and their structure. It has been demonstrated[11] that CA spectra are especially suited for the structure elucidation of *stable* gaseous ions with a lifetime of at least 10^{-5} s as both the peak width (kinetic energy release) and the relative abundances of the collision induced fragments are almost independent of internal energy variations.[11] Identical CA spectra are used as criterion for identical structures and vice versa.

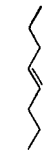
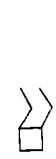
The CA spectra of nine isomeric cycloalkane molecular ions, $[C_8H_{16}]^{+\cdot}$, of varying ring size and length of the side chain are contrasted with those of 1-, 2-, 3- and 4-octene in Table I. No or little variation of the CA spectra with varying electron energy was observed.

It is evident from Table I that the CA spectra of the three-, four-, and five-membered rings and that of 1-octene are almost identical demonstrating that these molecular ions have isomerized almost completely[20] to a common structure (or a mixture of interconverting structures) prior to decomposition.[21] The length of the side chain has no influence on the isomerization behavior as shown with butylcyclobutane and 1,2-diethylcyclobutane. In contrast, the six-, seven-, and eight-membered rings show pronounced differences in their CA spectra which is especially apparent for the fragments at *m/e* 70, 81–83, 96, and 97. It is of special interest that for the three six-membered rings and the seven-membered ring the loss of the side chain is the dominant process demonstrating that the ring is intact prior to collision-induced decomposition which does not exclude that some decomposition processes procede via ring opening *during* decomposition. The differences in the CA spectra of cyclooctane and the smaller rings are less pronounced, although still distinct, as this compound has no side chain and will probably decompose via acyclic transition states.

The common structure to which 1-octene and the smaller rings isomerize could be (a) one of the smaller rings or (b) an unbranched or (c) a branched octene molecular ion. The CA spectra of a large variety of branched C_8H_{16} alkenes have been reported previously and differ considerably from that of 1-octene.[10] Similarly, the smaller rings can be ruled out as common intermediates as their spectra do not reflect the loss of the side chain as observed for larger rings. Excluding a nonclassical structure the present results suggest an octene molecular ion as common structure. To determine the radical site the CA spectra of 1-, 2-, 3-, and 4-octene were compared. While the CA spectra of 2-, 3-, and 4-octene are very similar, indicating a facile shift of the radical site with simultaneous hydrogen migration (as postulated in the literature[22]), that of 1-octene is distinct which is especially apparent for the fragments at *m/e* 41, 42, 82, and 83. This result shows that the stable 1-octene molecular ion with a lifetime of 10^{-5} s has not or not completely isomerized to a mixture of interconverting structures. An additional study of the field ionization kinetics and the metastable abundance ratios combined with ^{13}C labeling (not reported here[23]) demonstrates, however, that the 1-octene molecular ion must have isomerized to some extent to a mixture of double bond isomers under CA conditions.[10] Summarizing there is convincing evidence that alkylcycloalkane molecular ions with three-, four-, and five-membered rings and a lifetime of 10^{-5} s undergo ring opening to form initially the 1-alkene molecular ion, which isomerizes to some extent to a mixture of double bond isomers. Six-, seven-, and eight-membered rings, however, remain intact prior to decomposition. However, the results observed for the small rings do not necessarily apply also to unsubstituted cycloalkanes.[32]

Field Ionization Kinetics. The field ionization method allows us to study the decay of excited organic ions in the gas phase over the time range of 10^{-11}–10^{-5} s after ionization.[24] It will be demonstrated that this technique (which has been reviewed previously[12]) can be used to obtain both information on the

Table I. Collisional Activation Spectra of $[C_8H_{16}]^{+\cdot}$ Molecular Ions[a,b]

m/e													
27	4.2	4.1	3.6	2.4	1.2	2.0	2.2	1.7	1.6	1.3	1.6	1.1	1.9
29	3.0	3.5	4.1	2.0	1.2	1.8	1.8	1.4	1.2	1.1	1.2	1.0	1.3
39	5.6	5.4	5.0	3.3	2.0	2.7	3.1	2.7	2.6	2.4	2.7	2.3	3.6
41	14	13	10	7.6	5.7	6.2	7.1	6.5	5.2	4.2	5.4	4.3	6.5
42	4.1	4.2	3.8	2.4	1.8	1.8	2.3	2.3	2.3	2.0	1.5	2.1	4.0
43	1.6	1.8	1.8	1.1	0.8	0.9	1.0	1.2	1.0	0.9	0.8	1.0	2.0
51	0.7	0.7	0.5	0.4	0.3	0.4	0.3	0.4	0.3	0.3	0.4	0.3	0.4
53	2.2	2.2	2.0	1.4	1.1	1.1	1.3	1.3	1.1	1.0	1.2	1.0	1.1
54	3.0	2.6	2.6	1.7	1.3	1.3	1.6	1.7	1.2	1.2	1.8	1.3	2.0
55	9.5	8.5	9.9	7.1	5.8	4.5	5.4	6.4	7.6	9.2	8.6	6.0	6.5
56	5.9	6.2	7.8	5.9	5.8	5.2	5.6	5.8	3.0	2.5	1.4	3.4	7.6
57	1.9	2.1	2.6	2.2	2.6	2.8	2.7	2.5	1.0	0.6	0.3	1.3	1.6
65	0.6	0.5	0.3	0.3	0.3	0.2	0.3	0.4	0.2	0.2	0.3	0.2	0.2
67	2.5	2.4	1.7	2.0	1.5	1.3	1.5	2.0	1.4	1.2	2.8	1.4	2.0
68	2.0	2.4	2.5	1.7	1.5	1.4	1.5	3.0	1.7	1.0	0.8	1.8	4.1
69	5.6	7.2	4.8	4.7	4.3	3.1	3.6	5.4	3.7	3.4	2.7	3.6	7.7
70	12	12	12	15	16	15	14	13	5.7	2.1	0.7	5.6	10
71	0.8	0.8	0.8	1.1	1.1	1.2	1.1	1.1	0.5	0.3	0.1	0.5	1.3
77	0.3	0.3	0.2	0.2	0.1	0.2	0.2	0.2	0.3	0.2	0.3	0.2	0.2
79	0.6	0.5	0.3	0.3	0.3	0.2	0.3	0.3	0.3	0.3	0.6	0.3	0.3
81	1.0	0.8	0.6	0.6	0.5	0.4	0.4	0.5	0.6	0.7	1.2	0.7	0.5
82	2.9	2.9	3.4	6.5	8.0	7.2	7.1	7.6	6.0	0.6	32	5.2	4.6
83	11	10	13	17	20	19	17	18	10	1.6	32	9.7	15
84	5.3	5.7	6.1	10	13	12	11	12	3.2	1.1	–	5.4	11
95	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.3	0.5	0.1	0.2	0.1
96	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	1.1	3.6	–	7.2	0.2
97	1.2	1.3	1.4	2.5	3.4	3.3	3.1	2.9	37	56	0.2	33	4.0

[a] Abundances relative to the sum of all collision-induced fragments. [b] CA spectra taken at low electron energy were almost identical with those at 70 eV.

structure of cycloalkane molecular ions and the time scale for their isomerization. For the interpretation of the field ionization kinetic results it is important to remember that the dependence of the relative fragment intensities on the precursor ion lifetime reflects both differences in the kinetics of competing decomposition processes as well as structural changes prior to decomposition.

For a qualitative survey of the progress of the isomerization process with increasing time, field ionization mass spectra of all cycloalkanes were recorded as a function of the ion lifetime as described in the Experimental Section. As discussed above the calculated decomposition time varies to some degree within one spectrum; however, these variations are the same for all isomers. It has been demonstrated that metastable ion abundance ratios, although energy dependent to some extent, can be used to characterize ion structures.[25] Similarly the fragment ion abundance ratios in the time dependent field ionization spectra, discussed below, characterize the ion structure as a function of the ion lifetime. Again, identical fragment ion abundance ratios are used as criteria for identical structures.[26] This approach implies that the energy deposition function is similar for all compounds which seems to be approximately the case for such isomeric hydrocarbon molecular ions.

The field ionization mass spectra of 1-octene, *n*-pentylcyclopropane, *n*-butylcyclobutane, *n*-propylcyclopentane, and ethylcyclohexane for four different times ($t < 2 \times 10^{-11}$ s, $\sim 4 \times 10^{-11}$ s, $\sim 3 \times 10^{-10}$ s, and $\sim 10^{-5}$ s) are contrasted in Figure 1a-e. In ethylcyclohexane loss of the side chain with or without additional hydrogen rearrangement ($M^{+\cdot}-C_2H_5$ and $M^{+\cdot}-C_2H_6$) is by far the dominant process in all four spectra (Figure 1e) which clearly indicates that the six-membered ring remains intact over the entire time range. As expected the rearrangement process competes more effectively with the direct cleavage with increasing time as a result of both the lower activation energy and lower density of states in the activated complex.[27] (Similar results were obtained for the two dimethylcyclohexanes and methylcycloheptane.)

An entirely different time dependence is observed for 1-octene and the smaller rings: At the longest time the FI spectra of these compounds resemble each other closely[28] in support of the CA results that complete ring opening has occurred after 10^{-5} s. (It should, however, be stressed that the CA method samples predominantly stable ions and the FI technique reactive ions.) With decreasing ion lifetime the individual spectra become more distinct and at the shortest resolvable time ($t < 2 \times 10^{-11}$ s) pronounced differences are observed between all spectra. It is of special interest that in *n*-propylcyclopentane the loss of the side chain (*m/e* 69) is by far the most abundant process at 2×10^{-11} s but is of vanishing intensity at 10^{-5} s demonstrating that at the shortest time decomposition occurs from the intact five-membered ring. However, with butylcyclobutane and pentylcyclopropane not the loss of the side chain (*m/e* 55 and 41, respectively) but the loss of C_2H_4 dominates at the shortest time (excluding *m/e* 29, which has been shown to be a field dissociation process[12a]). Falick and Burlingame[6] have shown for methylcyclopentane that at short decomposition times the loss of C_2H_4 contains exclusively the original ring atoms. Similarily, Meyerson et al.[4,5] demonstrated that under electron impact conditions the loss of C_2H_4 from methylcyclopentane, ethylcyclopentane, and methylcyclohexane originated exclusively or with high specificity from the ring. Extending their results to *n*-pentylcyclopropane and *n*-butylcyclobutane the abundant loss of C_2H_4 (*m/e* 84) in both spectra shows that at 10^{-11} s the three- and four-membered rings are intact *prior* to decomposition. Summarizing the field ionization mass spectra as a function of the ion lifetime demonstrates that

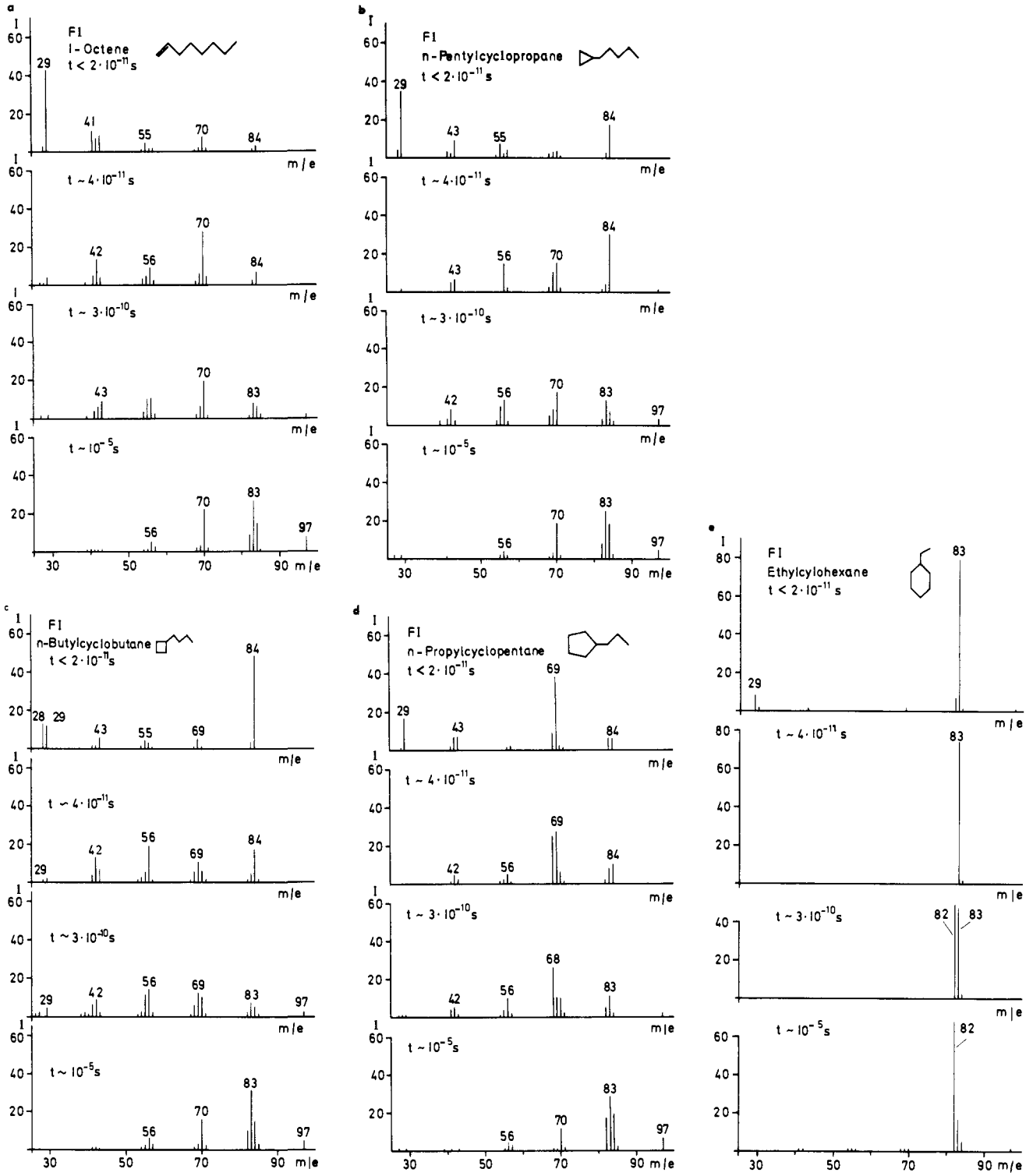


Figure 1. Field ionization mass spectra of cycloalkane molecular ions at $t < 2 \times 10^{-11}$ s, $\sim 4 \times 10^{-11}$ s, $\sim 3 \times 10^{-10}$ s, and $\sim 10^{-5}$ s after ionization. Abundances relative to the sum of all fragments. The decomposition time is calculated for *m/e* 69 (see Experimental Section).

at 10^{-11} s after ionization decomposition occurs from the intact three-, four-, and five-membered rings which open up at longer times.

The time scale for the isomerization of small cycloalkane rings can be studied in a more quantitative fashion by determining the relative rates of formation, di/dt, as a function of the ion lifetime. Rates of formation have been determined for all major fragments observed in the FI spectra of 1-octene, *n*-pentylcyclopropane, *n*-butylcyclobutane, and *n*-propylcyclopentane.[29] For the sake of clarity the following discussion will be restricted to two competing decompositions from each molecular ion, as illustrated in Figure 2a-e. Figure 2a-c contrasts the relative rates of formation of *m/e* 84 (loss of C_2H_4) and *m/e* 70 (loss of C_3H_6) from 10^{-11} to 10^{-5} s for 1-octene, *n*-pentylcyclopropane, and *n*-butylcyclobutane. As discussed above C_2H_4 is directly eliminated from the ring at short times while loss of C_3H_6 should be a rearrangement reaction. At the longest times ($\sim 10^{-5}$ s) similar ratios for the relative rates of *m/e* 70 and 84 are observed for all compounds in support of extensive or complete isomerization to a common intermediate. This ratio is, however, reversed at the shortest times ($\sim 10^{-11}$ s) for the three- and four-membered ring indicating decom-

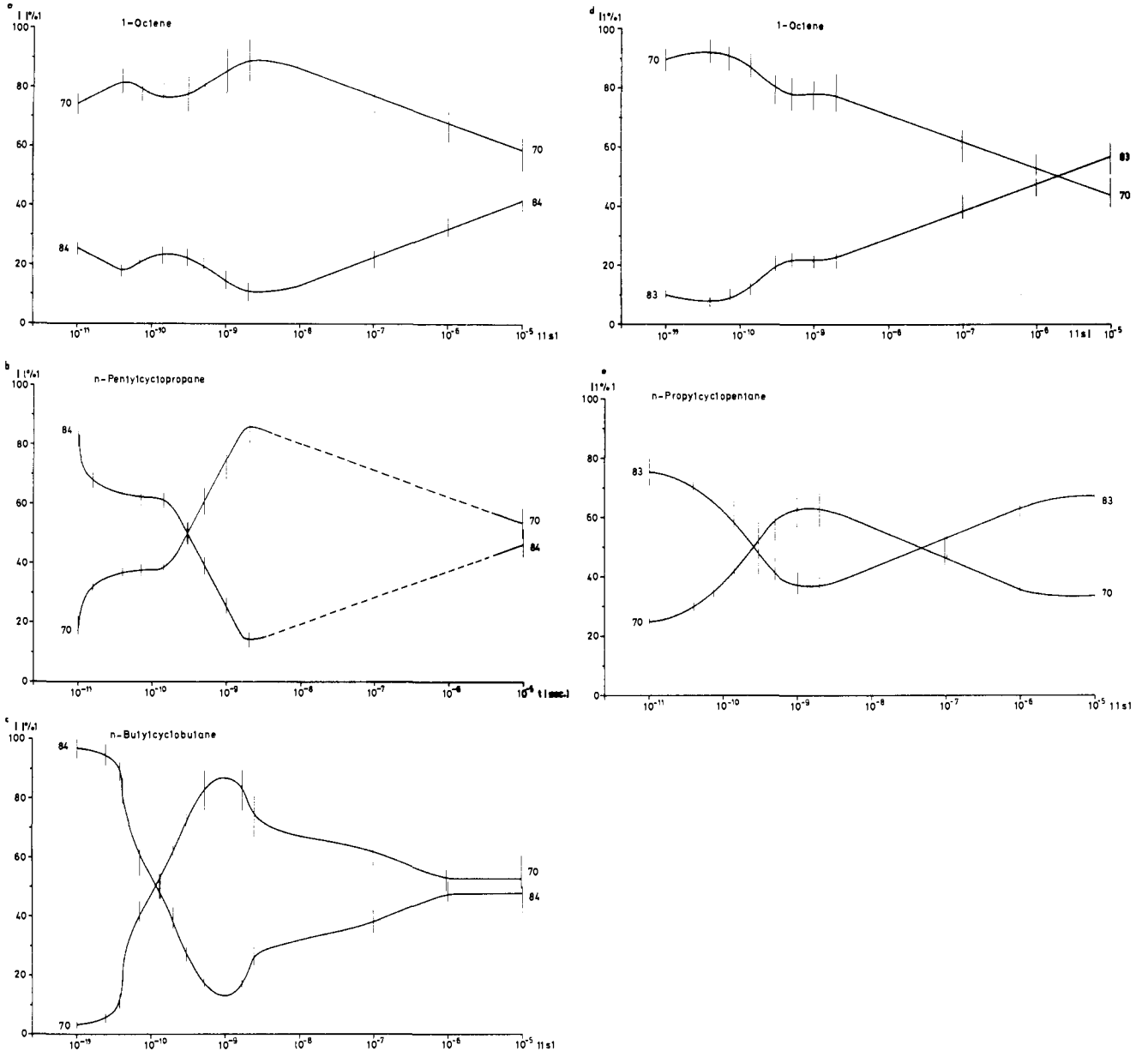


Figure 2. Relative rates of formation of *m/e* 84 and 70 from the molecular ions of 1-octene (a), *n*-pentylcyclopropane (b), and *n*-butylcyclobutane (c), and relative rates of formation of *m/e* 83 and 70 from the molecular ions of 1-octene (d) and *n*-propylcyclopentane (e).

position from the intact ring. Of special interest are the crossings in Figures 2b and 2c. They can be readily explained assuming that the rings have opened up at about 10^{-9} s, while at shorter times decomposition occurs predominantly from the intact ring. It is plausible to assume that the direct expulsion of ethylene from the ring has a higher density of states in the activated complex than the loss of propene by rearrangement explaining its higher relative rate at the shortest times. However, as a result of its lower activation energy the rearrangement competes more effectively with the direct expulsion of C_2H_4 at longer times. At about 10^{-9} s the ring opens up to form 1-octene and thus similar relative rates are observed at longer times.

The loss of ethylene is a less characteristic process in *n*-propylcyclopentane. Thus, in this case the competing formation of *m/e* 83 (loss of ethyl by direct cleavage) and *m/e* 70 (loss of propene by rearrangement) was contrasted with the corresponding processes in 1-octene. Again the decomposition curves show pronounced differences at times $<10^{-9}$ s reflecting the initially different structures. The loss of C_2H_5 by direct cleavage from the original *n*-propylcyclopentane molecular ion is the dominant process at 10^{-11} s while the rearrangement reaction (*m/e* 70) becomes more abundant at longer times (>5 $\times 10^{-10}$ s). At roughly 10^{-9} s the ring opens up to form the 1-octene molecular ion. At longer times the *n*-propylcyclopentane molecular ion behaves like the 1-octene ion as far as the *m/e* 83 and 70 competition is concerned.

The different kinetic behavior observed at times $<10^{-9}$ s between the cycloalkane and octene molecular ion must not exclusively result from the above discussed mechanistic differences but may simply reflect the fact that ring opening occurs within a spectrum of lifetimes ranging from 10^{-11} to 10^{-9} s after ionization which explains the observed crossings in Figure 2b, c, e equally well.

Thus, the decomposition curves presented above as well as additional data not reported here[29] suggest that three-, four-, and five-membered cycloalkane rings undergo ring opening within roughly 10^{-9} s.

Conclusions

There is convincing evidence from collisional activation and field ionization kinetic studies that alkylcycloalkane molecular

ions with three-, four-, and five-membered rings undergo ring opening after ca. 10^{-9} s to form initially 1-alkene molecular ions which, depending on the internal energy and ion lifetime, isomerize to some extent to a mixture of double bond isomers. From the identity of the CA spectra (reflecting to a large extent the stable ions) it can be concluded that the energy barrier for such ring opening processes is considerably smaller than the lowest threshold for decomposition and cannot exceed a few tenths of an electron volt.[30]

In contrast, cycloalkane molecular ions with six-, seven-, and eight-membered rings are stable *prior* to decomposition over the entire range of lifetimes and internal energies available in an electron impact mass spectrometer. As already pointed out by Meyerson et al.[4] for methylcyclopentane and methylcyclohexane the difference in the isomerization behavior is most simply accounted for as resulting from the difference in ring strain.

Furthermore the present results rule out that three- or four-membered cycloalkane molecular ions are formed by 1,3 or 1,4 elimination of HX from compounds of the general type RX (X = OH, F, Cl) as has been assumed sometimes in the past[31] which does not exclude that these eliminations proceed via transition states with a cycloalkane-like structure.

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Fluorine–Proton Overhauser Effects in Fluorine-Labeled Macromolecular Systems

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Abstract: Calculations of the $^{19}F\{^1H\}$ nuclear Overhauser effect in a system of nuclei corresponding to a *p*-fluorophenyl residue interacting with three linearly arrayed methylene groups have been performed as a function of the molecular correlation time (τ_c) and the distance (r) between the fluorine nucleus and the nearest methylene group. This collection of 11 nuclei is taken as a model for a fluoroaryl group covalently attached or reversibly complexed to a macromolecule, such that protons of the macromolecule can interact with the fluorine nucleus. Numerical results are presented which indicate the extent to which selective saturation of proton resonances of the macromolecule can be used to identify the interacting group; at 94.1 MHz selectivity diminishes for $\tau_c > 10^{-8}$ s and irradiation at any proton frequency (100 MHz) should lead to loss of fluorine signal intensity.

Fluorine-19 chemical shifts and coupling constants are often an order of magnitude larger than these parameters for a hydrogen nucleus in a similar situation and fluorine relaxation rates are potentially more sensitive to molecular environment than those for protons because of the importance of the chemical shift anisotropy mechanism. Coupled with a