hypochromism (i.e., association) in two pyrimidine-C_3-pyrimidine series, upon increasing alkyl group size, but *decreased quantum yields of dimerization.* (a) Replacing the 5-methyl group in T-C_3-T by ethyl: K. Golankiewicz and L. Strekowski, *Mol. Photochem.*, **4**, 189 (1972). (b) Increasing the size of the 3-alkyl group in bis-3-alkylated T-C_3-T derivatives: K. Golankiewicz and A. Zasada-Parzynska, *Bull. Acad. Pol. Sci.*, **22**, 945 (1974).

(35) The triplet 1,4 diradical which precedes dimer closes three times less efficiently for thymine than for uracil, a result attributed to the steric barrier of the 5-methyl group: P. J. Wagner and D. J. Bucheck, *J. Am. Chem. Soc.*, **92**, 181 (1970).

(36) Triplet derived dimers are quenchable and several arguments make short-lived triplet aggregates unlikely precursors in the unquenchable dimerization.[5c]

(37) There is no quenching by 0.1 M piperylene, the concentration of diene which is sufficient to trap all TMU triplets (cf. the ϕ_{isc} data) and is sufficient to trap all DMT triplets.[5c] Very high diene concentrations do give some quenching as do high concentrations of vinyl acetate and tetramethylethylene. This may be due to small amounts of singlet quenching or result from an interference with association. DMT singlet dimerization can be completely eliminated by CCl_4, presumably through a charge-transfer quenching mechanism: D. Murcia, R. Kleopfer, R. Maleski, and H. Morrison, *Mol. Photochem.*, 4, 513 (1972).

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(43) The aggregation mechanism does lead to one conclusion which is unexpected and deserving of further study. For organic media, one can estimate that a K_a greater than about 0.2 M^{-1} should have been detectable by osmometry; to accommodate values less than this, the ϕ_{DF}'s observed require that F_{ex} exceed 0.36 in organic solvents.

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Isomerization of Linear Octene Cations in the Gas Phase[1]

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Abstract: Using high-resolution electron impact data, metastable ion characteristics, collisional activation spectra, and field ionization kinetic measurements in conjunction with ^2H and ^{13}C labeling it is demonstrated that the decomposing molecular ions of 1-, 2-, 3-, and 4-octene isomerize to a mixture of interconverting structures within 10^{-9} s after ionization, while isomerization of the nondecomposing ions is incomplete. The energy barrier for this isomerization seems to be higher for 1-octene than for the other octenes. At the shortest resolvable ion lifetime ($\sim 2 \times 10^{-11}$ s) 1-octene molecular ions fragment predominantly by specific mechanisms while the decomposition becomes unspecific at $t > 10^{-10}$ s. As a result $CH_3\cdot$, $C_2H_5\cdot$, and C_3H_6 are eliminated in similar ratios from both ends of the molecular ion after $\sim 10^{-9}$ s suggesting that the equilibration of double bond isomers is mainly due to radical site migration accompanied by hydrogen rearrangements, which, however, do not involve the terminal hydrogens to a larger extent. At long ion lifetimes skeletal rearrangements are only pronounced prior to ethylene loss, but of lesser importance for other fragments originating directly from the molecular ion. In contrast, heptenyl ions, generated by methyl loss from 1-octene, decompose after complete randomization of all carbons.

The molecular ions of small alkenes (propenes and butenes) as well as the isomeric cycloalkanes with sufficient internal energy to undergo decomposition ("reactive" ions) isomerize to a common structure or a mixture of interconverting structures *prior* to decomposition as shown by ^2H and ^{13}C labeling,[3] metastable ion characteristics,[4] heats of formation data,[5] and field ionization kinetic measurements,[6] while the nondecomposing ions retain partially their original structure.[7,8] Such isomerization processes are, however, incomplete or negligible in larger alkene ions independent of the internal energies and ion lifetimes.[9-11] Apparent exceptions are the molecular ions of those alkenes differing only in the position of the double bond where it has been assumed that facile migration of the radical site (accompanied by hydrogen rearrangement) leads to an equilibration between the various double bond isomers making a location of the double bond by means of mass spectrometry difficult.[12] To shed further light on the details of this isomerization process we studied 1-, 2-, 3-, and 4-octene (in the trans configuration) with various techniques (electron impact (EI), metastable ion (MI) characteristics,[13] collisional activation (CA),[14] and field ionization kinetics (FIK)[15] in conjunction with ^2H and ^{13}C labeling).

Experimental Section

Instrumental Details. High-resolution EI data were obtained with a Varian MAT 711 double focusing instrument at the resolution of $M/\Delta M$ = 25 000 (electron energy 70 eV, electron beam 800 μA, source temperature 200 °C). They are the means of five individual measurements. MI and CA spectra were run on a double focusing mass spectrometer of reversed geometry constructed by us (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, electron beam 30 μA, source temperature ca. 150 °C). The technique for taking and evaluating CA spectra has been described previously.[9,14,16] All data are the means of at least two measurements.

An instrument of identical geometry, but equipped with a nonfocusing FI source, was used for ion lifetime measurements and for FI-CA measurements.[35] (With all three instruments samples were introduced via the indirect inlet system). Complete mass spectra as function of the ion lifetime were obtained by increasing the voltage

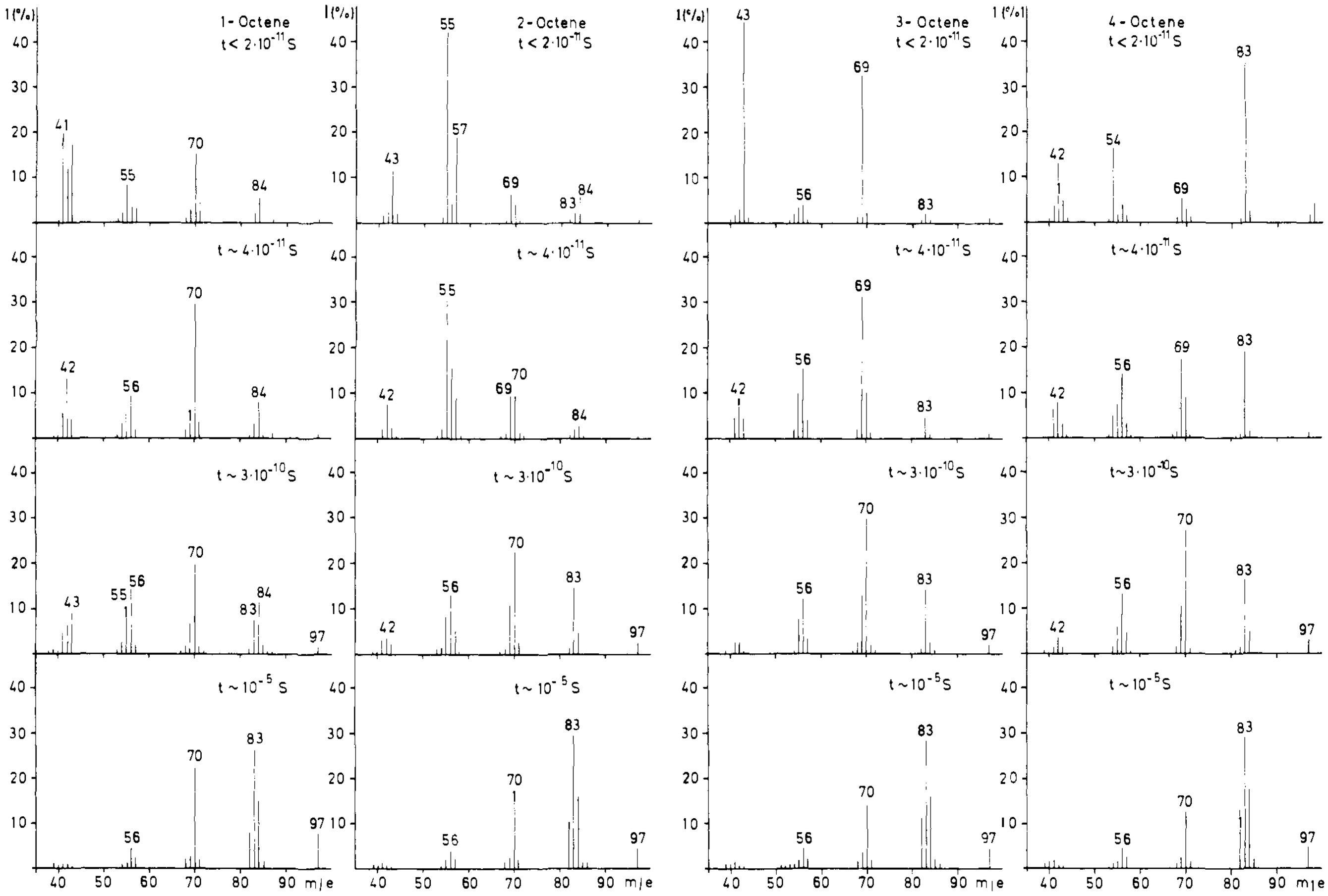


Figure 1. Field ionization mass spectra as function of the ion lifetime for 1-, 2-, 3-, and 4-octene (normalized to the sum of all fragments and corrected for natural ^{13}C contribution).

at the anode stepwise and scanning the magnet each time over the mass range of interest. All spectra are the means of at least three measurements. As the calculated ion lifetime depends on the mass of the fragment ion it also varies to some extent within one spectrum. The ion lifetimes given in Figure 1 have been calculated for m/e 70. They are shorter for smaller fragments and vice versa. From the individual data of such spectra rates of ion formation, di/dt, were calculated for all major fragments. Lifetimes were calculated off-line with a PDP 8e computer. For further instrumental details, the experimental procedure, and the lifetime calculations, see ref 16 and 17.

Materials. 1-Octene-*8*-^{13}C and 1-Octene-*8*-^2H. The commercially available 5-hexen-1-ol was converted by chain prolongation into 6-hepten-1-ol using conventional methods. 6-Hepten-1-ol was transformed into the corresponding iodide with methyltriphenoxyphosphonium iodide (MTPI) in hexamethylphosphoric acid triamide (HMPA).[18] Grignard reaction with $^{13}CO_2$ and CO_2 gave the acids $CH_2{=}CH(CH_2)_5{}^{13}COOH$ and $CH_2{=}CH(CH_2)_5COOH$ from which the corresponding alcohols were obtained by reduction with $LiAlH_4$. These were transformed into the iodides with MTPI/HMPA. Finally, reaction with $NaBH_3CN$ or $NaBD_3CN$ gave the desired olefins, with an isotopic purity of 91% in the case of 1-octene-*8*-^{13}C and 98% for 1-octene-*8*-^2H.

1-Octene-*1,1*-$^2H_2$. The compound was synthesized by Wittig reaction from heptanal using trideuteromethylphosphonium iodide with an isotopic purity of 79% (17% singly labeled and 4% unlabeled compound).

Results and Discussion

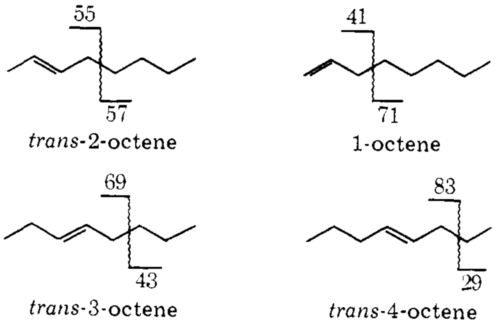
Metastable Ion and Collisional Activation Spectra. Ionization of an alkene molecule predominantly leads to a removal of an electron from the π orbital. If the resulting radical site remains localized at the original position prior to fragmentation preferential cleavage of the allylic carbon-carbon bond (α-cleavage)[19] should occur with or without charge migration to the alkylic moiety giving rise to prominent fragment ions as depicted in Scheme I for 1-, 2-, 3-, and 4-octene.

Table I. Metastable Ion Spectra of the Molecular Ions of Linear Octenes[a,b]

m/e	56	57	70	82	83	84	97
1-Octene	3	4	17	20	32	20	5
2-Octene	3	4	16	21	31	19	6
3-Octene	3	4	16	22	32	19	5
4-Octene	3	4	17	21	32	19	5

[a] The precursor ions were generated by EI. [b] The intensities are normalized to the sum of all fragments.

Scheme I



The published 70-eV EI spectra[20] do not show the expected fragmentation behavior supporting the assumed migration of the radical site.[21] This conclusion is corroborated by the MI spectra of the four linear octenes (Table I). Although the relative abundance of fragments may not only reflect the ion structure, but also variations in the internal energy,[22] such differences in the internal energy distribution apparently do not exist in double bond isomers as identical MI spectra—both in the relative abundances and peak widths (kinetic energy release)—are observed for all four linear octenes. This demonstrates that the molecular ions with sufficient energy for decomposition have completely isomerized to a mixture of interconverting structures within a lifetime of 10^{-5} s. This conclusion does not necessarily apply also for the nondecomposing octene ions which have a range of internal energies from zero up to the lowest threshold for decomposition. The structure of such "stable" ions can be characterized by their CA spectra as first demonstrated by McLafferty.[14] Thus, the CA spectra of the four octene ions generated on the one hand by electron impact and on the other hand by field ionization have been measured. Part of these spectra has been published previously;[16] the remainder is available on microfilm. The results demonstrate that while the CA spectra of the 2-, 3-, and 4-octene molecular ions generated by EI are almost identical within the reproducibility (±8%), demonstrating that also the large majority of the stable ions must have isomerized, they are distinct from that of 1-octene (see *m/e* 41, 70, 82–84, and 97).[33] Thus, the isomerization barrier between the 1-octene ion, on the one hand, and the 2-, 3-, and 4-octene ions, on the other hand, seems to be much higher than the barriers between the remaining octenes.[34] This is even more apparent when the CA spectra of the molecular ions generated by FI are compared. As a result of the extremely low internal energy of field ionized molecules the fractions of stable isomers which have already isomerized prior to collision is further reduced leading to more pronounced differences in the relative abundances.[23] It should finally be noted that the fragments due to allylic cleavage (which reflect the original structure, as shown below) are slightly enhanced in the spectra of 2-octene (*m/e* 55) and, especially, 3-octene (*m/e* 69) indicating that there exists also a finite energy barrier for interconversion between these isomers. CA spectra of a variety of branched octenes published previously[9] differ considerably from those of the linear octenes suggesting that upon isomerization the latter retain largely their linear structure, although the presence of a smaller fraction of branched species in the mixture of interconverting structures cannot be ruled out completely.

Ion Lifetime Measurements. Information both on the initial structure of gaseous ions as well as the time scale for their isomerization can be obtained from ion lifetime measurements[6,16] which have been carried out using the FIK method.[15] This technique permits a time-resolved study of unimolecular decomposition processes of gaseous organic ions from 10^{-11} to 10^{-5} s after ionization. For the interpretation of such ion lifetime measurements it is important to remember that the dependence of the relative fragment intensity on time reflects both mechanistic differences of competing decomposition processes as well as structural changes *prior* to decomposition. Such structural changes become evident if the fragmentation of isomeric ions is compared as a function of the ion lifetime. Two different experimental approaches were used to study the time dependence of the isomerization process of linear octenes.

(a) For a qualitative survey on the isomerization process complete field ionization mass spectra were recorded for different times using a technique described previously.[16]

(b) Normalized rates of formation were determined for several fragments giving a quantitative insight into the isomerization process.

FI mass spectra as function of the ion lifetime (normalized to the sum of all fragments) represent time-dependent metastable ion characteristics. Thus they immediately reflect the ion structure as function of the ion lifetime as long as differences in the internal energy can be neglected. As discussed above the latter assumption seems to hold for linear octenes.

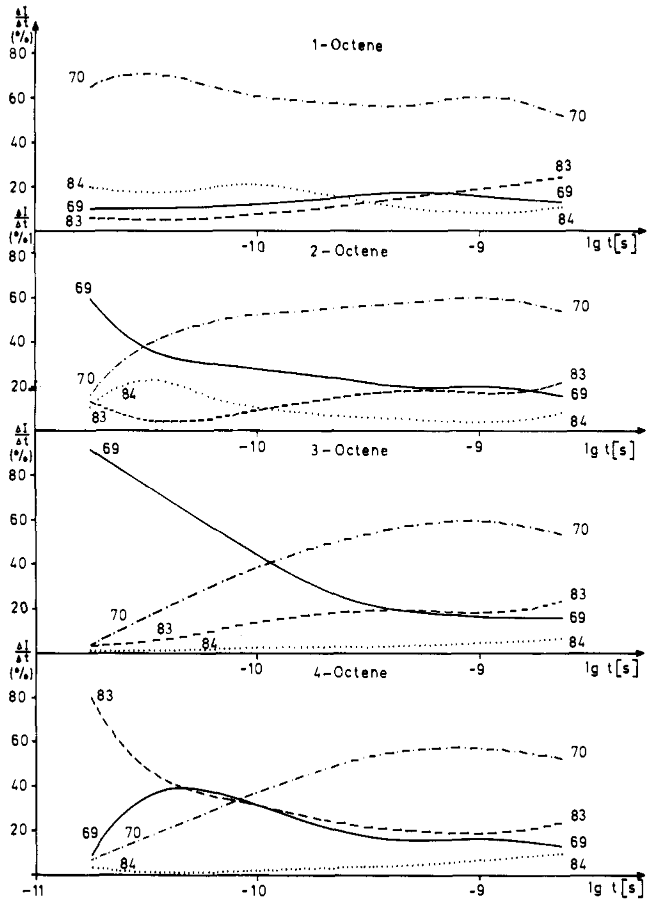


Figure 2. Relative rates of formation of $[C_5H_9]^+$ (*m/e* 69), $[C_5H_{10}]^{+\cdot}$ (*m/e* 70), $[C_6H_{11}]^+$ (*m/e* 83), and $[C_6H_{12}]^{+\cdot}$ (*m/e* 84) as function of the ion lifetime for 1-, 2-, 3-, and 4-octene.

Figure 1 contrasts the FI spectra of 1-, 2-, 3-, and 4-octene for four lifetimes ($<2 \times 10^{-11}$, $\sim 4 \times 10^{-11}$, $\sim 3 \times 10^{-10}$, and $\sim 10^{-5}$ s).[16] At $\leq 2 \times 10^{-11}$ s after ionization the fragmentation pattern of the four linear octenes differs drastically. The dominant fragments are formed by allylic cleavage with or without charge migration as depicted in Scheme I (*m/e* 41 in 1-octene,[36] *m/e* 57 and 55 in 2-octene, *m/e* 43 and 69 in 3-octene, and *m/e* 29 and 83 in 4-octene[24]) which clearly demonstrates that at this shortest time decomposition occurs predominantly from the original structure which should resemble qualitatively that of the neutrals. (Similar arguments have been used by Morgan and Derrick to conclude that 1- and 2-butene ions retain their original structure within 2×10^{-11} s after ionization[6]). With increasing ion lifetime the spectra become more similar and resemble each other closely at 10^{-5} s[25] demonstrating that the isomerization is complete within this time interval.

Rates of formation, $\Delta i/\Delta t$, were determined as a function of the ion lifetime for all abundant fragments. In Figure 2 the rates of four selected fragments (*m/e* 69, 70, 83, and 84), normalized to their sum, are shown for the time interval of 2×10^{-11} to 3×10^{-9} s. Although only two of the structurally significant α-cleavage products are among the selected ions, pronounced differences in the relative rates of formation are observed at the shortest time supporting that decomposition occurs from the initial structure of the molecular ions. Within the limited reproducibility the ratio of the relative rates becomes identical at $\sim 10^{-9}$ s for all four octenes. Although the rates of the various fragments relative to each other still vary as times goes on, these variations are the same for all four isomers down to a lifetime of 10^{-5} s. This result demonstrates that the isomerization process is complete after $\sim 10^{-9}$ s.

Fragmentation of ^{2}H- and ^{13}C-Labeled 1-Octene. In further support of the conclusions reached so far from MI, CA, and

Table II. Distribution of ^{13}C in Important Fragments Formed from 1-Octene-*8*-^{13}C under Electron Impact[a]

Loss of[b] $\left(\% \text{ of } \sum_{40}^{97}\right)$	Ion formed	Exptl	Stat[c]
$CH_3\cdot$	$[C_7H_{13}]^+$	42.6	12.5
(0.9)	$[C_6{}^{13}CH_{13}]^+$	57.4	87.5
C_2H_4	$[C_6H_{12}]^{+\cdot}$	23.2	25.0
(3.2)	$[C_5{}^{13}CH_{12}]^{+\cdot}$	76.8	75.0
$C_2H_5\cdot$	$[C_6H_{11}]^{+\cdot}$	60.9	25.0
(5.8)	$[C_5{}^{13}CH_{11}]^{+\cdot}$	39.1	75.0
C_2H_6	$[C_6H_{10}]^{+\cdot}$	65.2	25.0
(1.8)	$[C_5{}^{13}CH_{10}]^{+\cdot}$	34.8	75.0
C_3H_6	$[C_5H_{10}]^{+\cdot}$	40.8	37.5
(12.4)	$[C_4{}^{13}CH_{10}]^{+\cdot}$	59.2	62.5
$C_3H_7\cdot$	$[C_5H_9]^+$	53.8	37.5
(6.9)	$[C_4{}^{13}CH_9]^+$	46.2	62.5
C_4H_8	$[C_4H_8]^{+\cdot}$	37.8	50.0
(10.8)	$[C_3{}^{13}CH_8]^{+\cdot}$	62.2	50.0
$C_4H_9\cdot$	$[C_4H_7]^+$	68.2	50.0
(14.5)	$[C_3{}^{13}CH_7]^+$	31.8	50.0
$C_5H_9\cdot$	$[C_3H_7]^+$	40.9	62.5
(12.7)	$[C_2{}^{13}CH_7]^+$	59.1	37.5
C_5H_{10}	$[C_3H_6]^{+\cdot}$	51.5	62.5
(8.0)	$[C_2{}^{13}CH_6]^{+\cdot}$	48.5	37.5
$C_5H_{11}\cdot$	$[C_3H_5]^+$	66.4	62.5
(13.7)	$[C_2{}^{13}CH_5]^+$	33.6	37.5

[a] Measured at $(M/\Delta M)$ 10% = 25 000. All intensities are corrected for natural ^{13}C contribution and incomplete labeling. [b] For the unlabeled compound. [c] Calculated for random distribution of all carbons.

Table III. Metastable Decomposition of Heptenyl Ions Generated by $CH_3\cdot$ Loss from Differently Labeled 1-Octenes[a]

Loss of (% total fragment)	*m/e*	*8*-^{13}C (**1a**)		*8*-^2H (**1b**)	
		Exptl	Stat[b]	Exptl	Stat[c]
Ethylene	69	29	28.6	33	30.8
(44.5)	70	71	71.4	67	69.2
Propene	55	42	42.9	48	46.2
(55.5)	56	58	57.1	52	53.8

[a] The precursor ions were generated by EI. [b] Calculated for random distribution of all carbons. [c] Calculated for random distribution of all hydrogens.

FIK data on the isomerization of linear octenes the fragmentation of the molecular ions of 1-octene (**1**), 1-octene-*8*-^{13}C (**1a**), 1-octene-*8*-$^2H_1$ (**1b**), and 1-octene-*1,1*-$^2H_2$ (**1c**) were studied under EI and FI conditions. This is the first study of labeled 1-octene and is, thus, of interest beyond the specific problem of the equilibration of double bond isomeric molecular ions discussed here.

Electron Impact Studies. The Molecular Ion. Table II summarizes the label distribution in all important fragments formed by EI from **1a**. The results demonstrate that the fragments are neither formed by specific mechanisms from the initial structure of the 1-octene molecular ion nor are they consistent with a random distribution of all carbon atoms as expected if a complete equilibration of the linear structure with one or several branched structures would have occurred. Moreover, the ^{13}C distribution does not necessarily result from a skeletal rearrangement *prior* to or during decomposition, but may be explained by a direct bond cleavage from both ends of the carbon skeleton preceded by hydrogen migration. Thus, the detection of skeletal rearrangements necessitates the use of differently labeled compounds. In a study of the EI induced decomposition of multiply ^{13}C-labeled 1-heptenes Falick and Gäumann[11] demonstrated that the loss of ethylene was indeed preceded by substantial skeletal rearrangements. However, for all other fragments originating directly from the molecular ion skeletal rearrangements were less pronounced (10–20%). Their results should qualitatively also apply to the decomposition of 1-octene. It is open to question whether these skeletal rearrangements precede a specific cleavage of the carbon skeleton, thus leading to branched or cyclic isomers *prior* to decomposition, or whether rearrangement occurs *during* decomposition of the linear octene ion (e.g., via transition states of branched or cyclic configuratons). In conjunction with Falick and Gäumann's data[11] our results support our earlier conclusion that octene molecular ions undergo only partial *skeletal* isomerization. Moreover, the data are consistent with, but do not prove, an extensive hydrogen migration prior to decomposition as expected for the postulated equilibration of double bond isomers.

Metastable Decomposition of Heptenyl Ions. The decomposition behavior of fragment ions differs considerably from that of the octene molecular ions as demonstrated with $[C_7H_{13}]^+$ ions. Methyl loss from 1-octene leads to a heptenyl fragment, $[C_7H_{13}]^+$. This is the only fragment in the low-resolution mass spectra of **1a** and **1b** with a pure isotopic composition, thus allowing to study the further fragmentation. Table III summarizes the metastable decomposition of heptenyl ions, formed by loss of $CH_3\cdot$ from **1**, **1a**, and **1b**. The data demonstrate that complete randomization of all carbons and almost complete randomization of all hydrogens[26] is observed in support of previous conclusions, based on CA[9] and MI[27] spectra, that alkenyl ions undergo complete isomerization to a mixture of interconverting structures *prior* to decomposition.

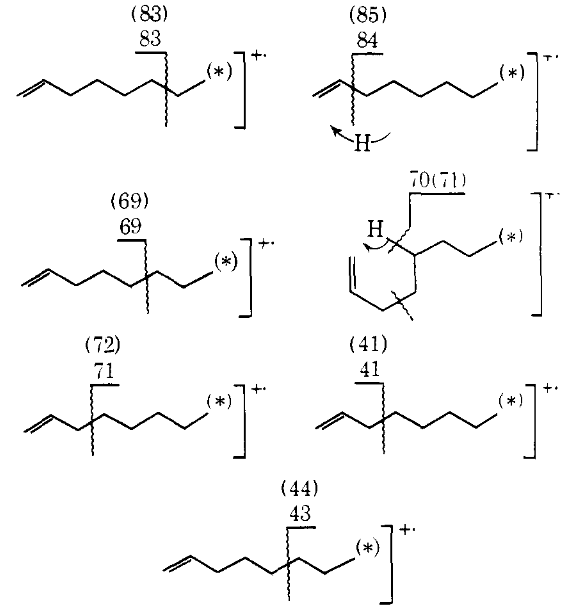
Ion Lifetime Measurements of ^2H- and ^{13}C-Labeled 1-Octenes. The EI measurements revealed a complex breakdown of 1-octene molecular ions. Hoping to unravel these fragmentations and to shed further light on the postulated equilibration of double bond isomers the decomposition of the molecular ions of **1a**, **1b**, and **1c** has been studied as a function of the ion lifetime.

C_7 Ions. At $t < 2 \times 10^{-11}$ s only 47 ± 6% of the methyl lost from **1a** and 52 ± 6% of that lost from **1b** contained the C-8 atom. For longer times values scattering around 50% are found for both compounds reaching 46 ± 6% for **1a** and 45 ± 6% for **1b** at 1×10^{-5} s after ionization. As a result of the low intensity of this process and uncomplete labeling (vide infra) the data for **1c** are less reliable demonstrating that at the shortest time at least 30% of the methyl lost contained C-1. This result demonstrates that already at the shortest time methyl is mainly lost from both ends of the molecular ion. Roughly half of the molecular ions expel the C-8 atom by direct cleavage while at least one-third loose the C-1 atom. The latter process must be accompanied by a very fast H shift. While the extent of methyl loss from the terminal positions of 1-octene does not change significantly with time, Falick and Gäumann[28] observed a decreasing participation of the terminal positions for methyl loss from 1-hexene with increasing time. It is further noteworthy that the label loss from **1a** and **1b** is identical within the reproducibility from 10^{-11} to 10^{-5} s, demonstrating that there is no "scrambling" of the terminal hydrogens over the entire time range.

C_6 Ions. The relative abundance of fragment ions containing six carbons, normalized to their sum, is shown in Figure 3 as a function of the ion lifetime (2×10^{-11} to 3×10^{-9} s) for **1**, **1a**, **1b**, and **1c**. While the data for **1a** and **1b** are corrected for incomplete labeling the values for **1c** are only corrected for unlabeled material, but not for 17% singly labeled molecules.

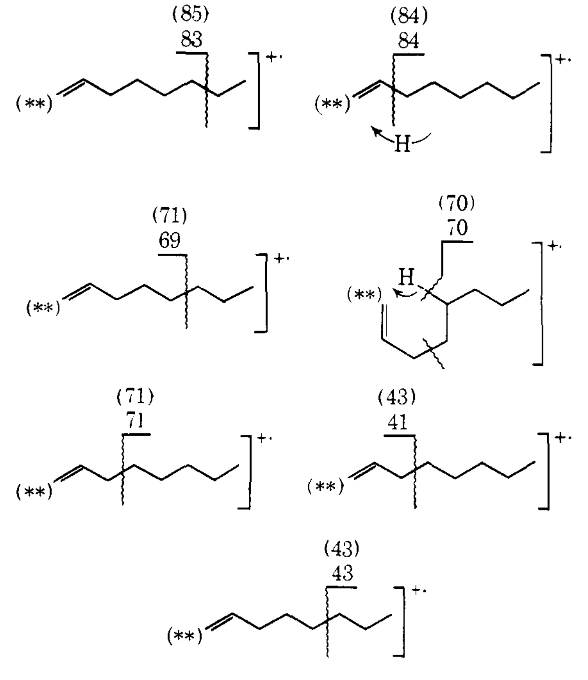
The decomposition at the shortest time will be discussed first. Here the data for **1c** can be corrected for the contribution from the singly labeled compound based on the assumption of a specific decomposition at this time (vide infra). The following discussion is based on these corrected data. Figure 3 demonstrates that at 2 × 10^{-11} s *m/e* 84 (loss of ethylene) is almost completely shifted to *m/e* 85 in **1a** and **1b**, but remains to a large extent *m/e* 84 in **1c**, proving that at this shortest resolvable time ethylene loss occurs with a high specificity from the unsaturated end of the molecule (Schemes II and III) although no information on the origin of the transferred hydrogen is available. On the other hand, *m/e* 83 (loss of an ethyl radical) remains at *m/e* 83 in **1a** and **1b**, but is completely shifted to *m/e* 85 in **1c**. Thus, ethyl is exclusively lost from the saturated end of the molecule by simple bond cleavage. The ethyl and ethylene elimination become noticeably unspecific only after ~10^{-10} s after ionization, both unspecific processes yielding an *m/e* 84 in **1a** and **1b**, but an *m/e* 83 and 86 in **1c**. At 1.7 × 10^{-9} s after ionization 47 ± 5% of the ethyl lost contains C-8 and 43 ± 5% C-1, the remainder coming from central parts of the molecular ion.[29] These values do not change significantly at longer times (at 1 × 10^{-5} s still 43% of the ethyl lost contains C-1). Ethyl loss from the unsaturated end of the molecule must be preceded by hydrogen shifts pointing at a radical site migration.

Scheme II[a]



[a] *m/e* values correspond to the unlabeled compound **1**, values in parentheses to the labeled compounds **1a** and **1b**. Position of the label is indicated by an asterisk.

Scheme III[a]



[a] *m/e* values correspond to the unlabeled compound **1**, values in parentheses to the labeled compound **1c**. Position of the label is indicated by an asterisk.

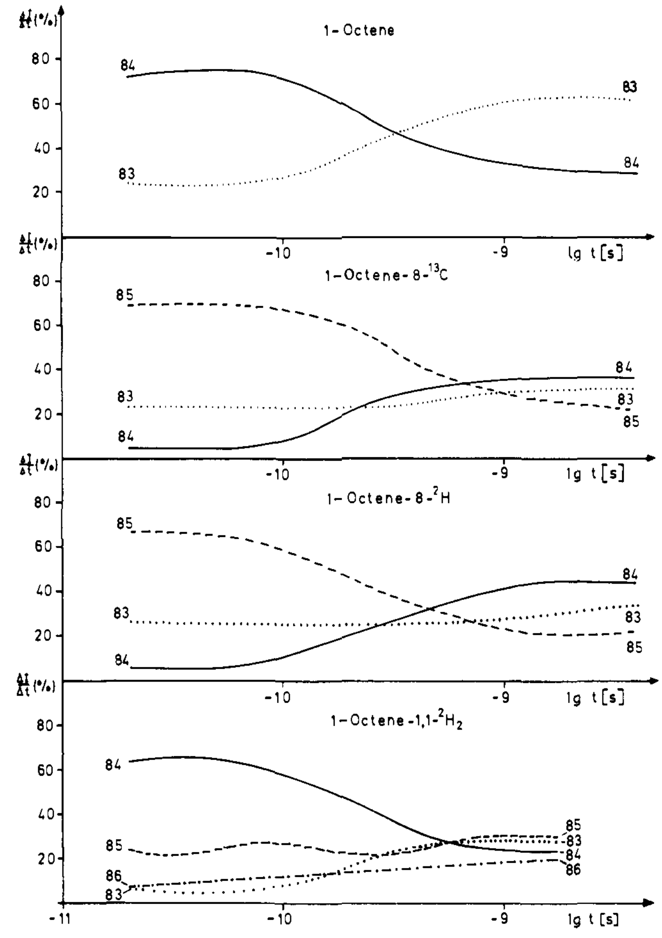


Figure 3. Relative rates of formation of $[C_6H_{11}]^+$ and $[C_6H_{12}]^{+\cdot}$ fragments (normalized to the sum of all C_6 fragments) from 1-octene (**1**), 1-octene-*8*-^{13}C (**1a**), 1-octene-*8*-$^{2}H_1$ (**1b**), and 1-octene-*1,1*-$^{2}H_2$ (**1c**) for 2 × 10^{-11} to 3 × 10^{-9} s after ionization.

While at long times ethyl is lost in almost equal proportions from both ends of the molecule, this is not the case for ethylene loss. At 1.7 × 10^{-9} s the $[C_6H_{12}]^{+\cdot}$ ion retains 84 ± 5% C-8 and 77 ± 7% C-1, i.e., at longer times ethylene is predominantly lost from the central part of the molecular ion by skeletal rearrangement. Substantial skeletal rearrangements for the ethylene loss from the molecular ion were also postulated by Falick and Gäumann in an FIK study[28] of 1-hexene and an EI study[11] of 1-heptene.

C_5 Ions. Figure 4 shows the relative intensities of fragments containing five carbons (again normalized to their sum) for **1**, **1a**, **1b**, and **1c**. At the shortest time (2 × 10^{-11} s) *m/e* 70 (propene loss) is completely shifted to *m/e* 71 in **1a** and **1b**, but remains to a large extent *m/e* 70 in **1c**, and thus can be explained as McLafferty analogue rearrangement with charge migration to the alkylic moiety (Schemes II and III). Similarily, *m/e* 71 is completely shifted to *m/e* 72 in **1a** and **1b**, but remains *m/e* 71 in **1c** (this peak being superimposed by the pentenyl ion, vide infra) demonstrating that *m/e* 71 is formed with high specificity by allylic cleavage with charge migration

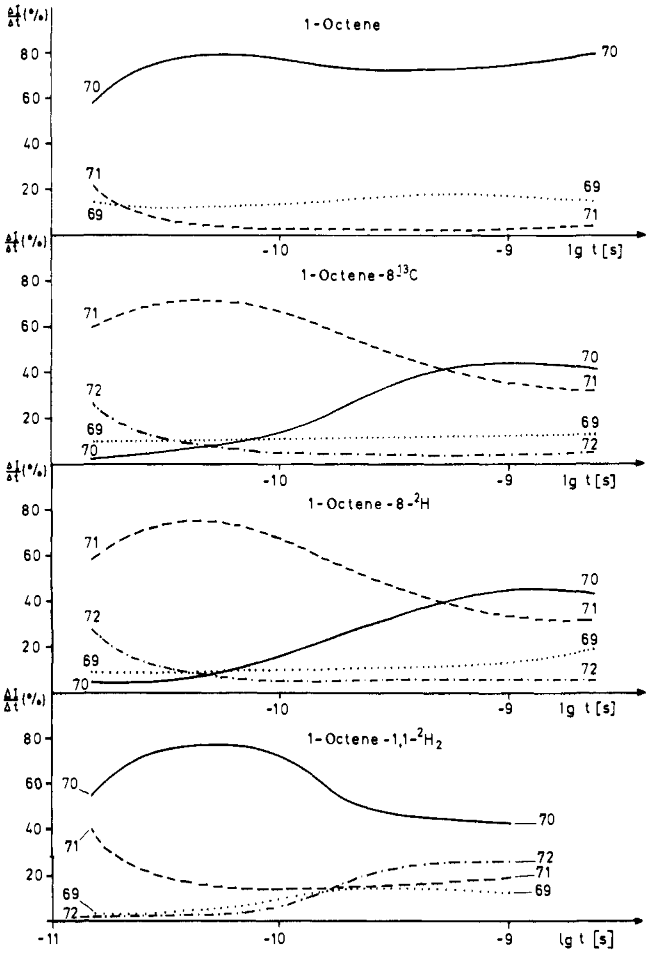


Figure 4. Relative rates of formation of $[C_5H_9]^+$, $[C_5H_{10}]^{+\cdot}$, and $[C_5H_{11}]^+$ fragments (normalized to the sum of all C_5 fragments) from 1-octene (**1**), 1-octene-*8-^{13}C* (**1a**), 1-octene-*8-$^2H_1$* (**1b**), and 1-octene-*1,1-$^2H_2$* (**1c**) for 2×10^{-11} to 3×10^{-9} s after ionization.

(Schemes II and III). Finally, *m/e* 69 remains largely (but not completely) at *m/e* 69 in **1a** and **1b**, but is shifted completely to *m/e* 71 in **1c**, demonstrating that also this ion is formed to a large extent by a specific mechanism at the shortest time (direct cleavage with charge retention at the unsaturated moiety of the molecule as depicted in Schemes II and III). The time dependence of these fragments parallels that of the C_6 fragments: they become unspecific only after roughly 10^{-10} s. Unspecific fragmentation gives rise to *m/e* 70 in **1a** and **1b**, but to *m/e* 72 and 69 in **1c**. As example, the propene elimination will be discussed for $t = 1 \times 10^{-9}$ s. At this time 47 ± 5% of the $[C_5H_{10}]^{+\cdot}$ fragments retain C-8 and 42 ± 5% C-1, i.e., after 10^{-9} s this fragment is again predominantly formed in about equal proportions by propene loss from both ends of the molecule and only to a smaller extent by propene loss from central parts of the molecular ion.

C_3 Ions. The label retention in C_3 fragments from **1a** has also been studied as a function of the ion lifetime. The data (available on microfilm) again reveal a high specificity at the shortest time for the formation of the propenyl and propyl ions becoming unspecific at slightly longer times.[30]

The lifetime measurements can be summarized as follows: up to ~10^{-10} s after ionization 1-octene molecular ions decompose mainly by specific mechanisms (as also reported by Falick and Gäumann for 1-hexene[28]) supporting that decomposition occurs from the original structure. Methyl loss is the only exception. Already at the shortest time this process occurs by two competing mechanisms from both ends of the molecular ion having still the original structure. At longer times pronounced skeletal rearrangements are only observed for the ethylene loss while most other fragments are predominantly formed by alkyl or alkene elimination from both ends of the molecular ion suggesting that radical site migration ("double bond" migration) must have preceded those decompositions. Such radical site migration leads to a complete equilibration of double bond isomers. In this context it is noteworthy that most fragments reach their maximum unspecificity at about 10^{-9} s after ionization which coincides with the time after which identical fragmentation is observed with 1-, 2-, 3-, and 4-octene, i.e., after which the isomerization is complete.

Figures 3 and 4 demonstrate that the hydrogen shifts necessary for such radical site migration do not involve the hydrogens at C-8 and only to a smaller extent those at C-1.[31] After radical site migration not only the hydrogens at C-8 but also those at C-1 are primary hydrogen atoms, which are less readily abstracted in hydrogen rearrangement reactions than secondary hydrogens,[32] which may explain why these hydrogens do not take part in the equilibration process.

Conclusions

MI spectra of 1-, 2-, 3-, and 4-octene molecular ions generated by EI demonstrate that the reactive ions have completely isomerized to a mixture of interconverting structures prior to decomposition. This result is corroborated by FIK measurements showing that the equilibration is already complete after 10^{-9} s. Surprisingly, about the same time interval is necessary for skeletal isomerization of C_4H_8 isomers[6] and cycloalkanes with small rings.[16]

CA spectra show that the isomerization among the nondecomposing ions is extensive but not complete. This conclusion holds especially for 1-octene, which seems to have a higher energy barrier for radical site migration than 2-, 3-, and 4-octene.[34]

Ion lifetime measurements of labeled molecules reveal that up to ~10^{-10} s after ionization 1-octene molecular ions decompose predominantly by specific mechanisms. At longer lifetimes some skeletal rearrangements are observed which are especially pronounced for ethylene loss. However, the small extent of skeletal rearrangements found for the other fragments does not explain the complete equilibration of double bond isomers. Rather, this equilibration can be rationalized by radical site migration accompanied by hydrogen rearrangements. In support of this assumption alkyl and alkene elimination from both ends of the molecular ion are observed at $t > 10^{-10}$ s. The hydrogen rearrangement necessary to explain such radical site migration, however, involves the terminal hydrogens only to a negligible extent. The exact mechanism for such radical site migration remains obscure. Although 1,3 hydrogen shifts leading to the successive formation of 2-, 3-, and 4-octene molecular ions would explain the observed isomerization most easily, other hydrogen transfer mechanisms may operate simultaneously.

The isotopic labeling data further support our earlier conclusion that alkene molecular ions show, if at all, only a partial *skeletal* isomerization, while such skeletal isomerization is complete with alkenyl fragment ions.

Finally, the analytical implications of the above discussed results are noteworthy. The characteristic fragmentation observed in the FI spectra of alkenes makes an immediate and unambiguous localization of the double bond possible, even in the absence of reference spectra.

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Supplementary Material Available: two tables (Collisional Activation spectra of the Molecular Ions of Linear Octenes and Label Retention of C_3-Fragment Ions from **1a** as Function of the Decomposition Time (2 pp). Ordering information is given on any current masthead page.

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(24) *m/e* 29 is the most abundant fragment in the spectrum. As this ion is partially formed by field dissociation at the shortest time,[15a] it has been omitted from all spectra.
(25) The remaining differences in the relative abundances are both due to the limited reproducibility of the FI data (see Experimental Section) and differences in the internal energy which may be more pronounced under FI than under EI conditions due to the different polarization of the molecule in the high electric field prior to ionization.
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(29) The data from **1c** were corrected for 17% singly labeled material assuming fragmentation from both ends of the molecular ion with equal probability and no H/D exchange at C-1.
(30) Unspecific fragmentation starts at a shorter time than for C_5 and C_6 ions, which may result from the fact that these ions are partially formed by a secondary decomposition. It has been shown above that complete randomization of all carbon atoms occurs *prior* to such secondary decomposition.
(31) Some H/D exchange at C-1 occurs at longer times and seems to be especially pronounced *prior* to $[C_5H_{10}]^{+\cdot}$ formation (*m/e* 70) where at 1×10^{-5} s loss of 34% $C_3H_4D_2$ and 54% C_3H_6, but also 12% C_3H_5D, from **1c** is observed.
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(33) Part of the fragments the abundance of which shows pronounced differences is also formed by unimolecular decomposition and, hence, may not only reflect the ion structure, but also differences in the internal energy as discussed previously.[14] The metastable ion spectra reported in Table I demonstrate, however, that the internal energy distribution must be identical or very similar for octene molecular ions. Hence the observed differences in the CA spectra exclusively reflect differences in structure.
(34) However, one of the referees pointed out that the observed differences in the CA spectra which reflect differences in rates need not necessarily result from a higher energy barrier in the isomerization between 1-octene and the other isomers, but may be due to different transition state geometries (entropy-like factors) or forbidden orbital symmetries for the rearrangement.
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Polar Effects in Radical Reactions. 7. Positive ρ Values for the Reactions of Isopropyl and *tert*-Butyl Radicals with Substituted Toluenes[1]

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Abstract: Hammett equation correlations are reported for the reaction of isopropyl radicals, generated by photolysis of azoisopropane, and *tert*-butyl radicals, generated by photolysis of either *t*-BuN=NBu-*t* or *tert*-butyl peroxypivalate, with a series of substituted toluenes at 30 °C. Rates of hydrogen abstraction from the toluenes were measured relative to deuterium abstraction from either benzenethiol-*d* or 2-methyl-2-propanethiol-*d*. A plot of log (relative rate constant) vs. σ constants gives for the isopropyl radical, $\rho = 0.8 \pm 0.1$, $s_y = 0.06$ (21 points); and for the *tert*-butyl radical, $\rho = 1.0 \pm 0.1$, $s_y = 0.04$ (23 points). The traditional "polar effects" interpretation of a Hammett equation correlation of an atom abstraction reaction and Zavitsas' recently proposed alternative explanation are discussed. The positive ρ values observed for the systems studied here prove the reality of substituent effects on polar resonance structures in the transition state (SETS). However, we believe that substituent effects on the bond dissociation energy (BDE) of the benzylic C–H bond are also important in these systems. Therefore, we suggest, in contrast to what is rather common practice in the literature, that *both* SETS *and* effects of substituents on BDE should be considered in explaining the results of Hammett equation correlations of these and other radical reactions.

The first observations of the sensitivity of radical reactions to polar substituents were published in 1945–1947. Mayo,[3] Price,[4] Bartlett,[5] and their co-workers postulated that dipolar resonance structures cause the transition states for certain radical reactions to be more stable than expected and that these polar structures markedly influence the reactivity patterns observed. In subsequent years, polar effects have been used to rationalize the tendency toward cross-termination reactions,