51. The Mass Spectra of Organic Compounds

7th Communication[1])

4,4-Dimethyl-1-Pentene

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Summary

Loss of $CH_3^{\cdot}$, CH_4, C_2H_4, $C_3H_5^{\cdot}$, C_3H_6 and $C_3H_7^{\cdot}$ from the molecular ions of a number of ^{13}C-labeled analogs of 4,4-dimethyl-1-pentene was studied both in normal (source) 70-eV electron impact (EI) spectra and in metastable spectra. For loss of $CH_3^{\cdot}$ in the source, 96% of the methyl comes from positions 5, 5′ and 5″, while the remainder comes from position 1. In the metastable spectra, loss of C-1 (16%) and C-3 (9%) is increasing in importance. The loss of ethylene is a particular case: either C-1 or C-3 are lost with any other C-atom from positions 2,5,5′, and 5″ (8 × 11%) in the metastable spectra, the probability for simultaneous loss of C-1 and C-3 being 6%. If C-1 seems to have a somewhat higher probability than C-3 for fragmentation within the source, these two positions become completely equivalent in the metastable time range. The *T*-values (kinetic energy release) for the different positions show small, but statistically different values and a small isotope effect. Loss of $C_3H_5^{\cdot}$ (allylic cleavage) is 100% C-1, C-2 and C-3, *i.e.*, no evidence for skeletal rearrangement is seen. This is also true for loss of C_3H_6 (*McLafferty* rearrangement) within the source, but in metastable decay the other positions gain in importance. The neutral fragment $C_3H_7^{\cdot}$ appears to be the result of consecutive loss of $CH_3^{\cdot}$ and C_2H_4, rather than a one-step loss of propyl radical or the inverse reactions sequence. No metastable reaction can be seen for this reaction. Decomposition of labeled $C_6H_{11}^+$ and $C_5H_{10}^{+\cdot}$ secondary ions occurs in an essentially random fashion.

Introduction. – A key point in studying rearrangements in a mass spectrometer is the question of whether the rearrangement occurs prior to or in concert with the neutral fragment loss. The observation of neutral losses involving atoms from several sites is not in itself sufficient evidence of prior rearrangement, since this result could be produced either by the presence of a symmetrical transition state or by multiple com-

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[1]) 6th Communication, see [1].

peting pathways (each of which might be completely specific) giving rise to the loss of the same neutral fragment. An example of the latter kind of behavior is the loss of C_3H_5 from ionized phenyl propylether [2], in which several parallel reactions with different transition state ring sizes occur, rather than 'scrambing' followed by C_3H_5-loss.

No firm evidence of multiple pathways involving skeletal rearrangement has yet been presented, although some suggestive evidence for this sort of behavior can be seen in the data for ethylene loss from alkenes containing six to nine C-atoms and some cycloalkanes [3–11]. Production of $(M-C_2H_4)^+$-ions appears to occur in these molecules in conjunction with more apparent skeletal rearrangement than in any other fragmentation. Yet both metastable decomposition data [12] [13] and collision-induced dissociation studies [14–16] of alkene isomers tend to show that ionized alkene isomers larger than pentene or hexene do not in general isomerize to a single isomer or mixture of interconverting structures and, in fact, that little isomerization of the molecular ions seems to occur. Thus it seems clear that the possibility of multiple competing reaction pathways involving skeletal rearrangement is deserving of further scrutiny.

In the work reported here, we have attempted to distinguish between the various possibilities for the loss of C_2H_4 from 4,4-dimethyl-1-pentene through the use of exhaustive ^{13}C-labeling. The decomposition of the molecular ions and some of the fragment ions was studied. Losses of fragments other than C_2H_4 were examined for evidence of prior rearrangement. Both fragmentations occurring within the ion source (normal spectra) and metastable decompositions (parent ion lifetimes of a few microseconds) have been studied in sufficient detail to characterize an array of individual component processes whose sum for example is 'loss of C_2H_4 from the molecular ion'.

In this work we make use of the following symbolism for the description of the loss of positions r, s or t to the neutral fragment.

C-r: indicates C-atom in position r
C(r): loss of the C-atom in position r to the neutral fragment
p(r): probability in percent for this loss
$C(r \cap s)$: simultaneous loss of positions r and s
$C(r \cap s \cap t)$: simultaneous loss of positions r, s and t
$C(r \cap s)'$ $(=C(r' \cap s')$, (or exclusive): loss of either position to the neutral fragment
$C(r \cap s \cap t)'$: loss of one (and only one) of the positions r, s or t to neutral fragment.

Experimental. – Electron impact (EI) mass spectra were obtained with a *CEC 21-110B* mass spectrometer coupled to a *PDP-12* computer. The ion source temperature was maintained at 120° and the electron energy was approximately 60 eV. Each spectrum was measured at least eight times and averaged.

Mass-analyzed ion kinetic energy (MIKE) spectra were recorded on a *VG-Analytical ZAB-2F* coupled to a *PDP-11* computer. Each of the metastable transitions was scanned (by sweeping the electric sector voltage) ten times and peak areas were averaged. Source temperature was 180° and an ionizing energy of 70 eV was used.

Synthesis. The general path for the synthesis of the labeled compounds has been described elsewhere [17] and the purity of the label positions has been confirmed in critical cases by NMR. However two steps in the reaction sequences merit special comments: firstly the chain prolongation of labeled *tert*-butyl halides with ethylene, where mixing of the label positions occured with $AlCl_3$ as catalyst, and secondly the transformation of neopentyl alcohol to the corresponding bromide that showed a particular bad yield. In the first case we replaced ethylene by methoxyethyl *p*-toluenesulfonate in Et_2O at 75° and $LiCuCl_3$ as catalyst and observed no positional exchange with a 36% chemical yield. In the second case we transformed neopentyl alcohol *via* the triethylneopentoxysilane to the bromide in a 50% overall yield [18]. All final products were purified by prep. GC and checked by analytical GC for expected impurities.

Isotopic purity of singly labeled materials was 91, 91, 90, 81 and 86% for molecules labeled in positions 1,2,3,4 and 5′, respectively. Isotopic purity of the 1,2-, 1,3-, 1,4- and 2,3- $^{13}C_2$-labeled analogs was 82, 83, 73, 79 and 80% $^{13}C_2C_5H_{14}$, respectively. Isotopic purity of 1,2,3-, 4,5,5′- and 5,5′,5″- was 64, 58 and 40% $^{13}C_3C_4H_{14}$, respectively, as measured by mass spectrometry. Unlabeled 4,4-dimethyl-1-pentene was obtained commercially *(Fluka)* and further purified by GC. After purification, all compounds were estimated to be 99% pure by GC.

Results. – The intensity of the major ions in % of the total ionization (TIC) is given in *Table 1* for both source and metastable spectra. *Table 2* reports the probabilities in % for the loss of a given position to the neutral fragment, calculated after correction of the spectra for incomplete labeling. If the loss of $C_3H_5^{\cdot}$ is the major fragmentation path in the ion source, this is no longer the case for the (slow) metastable decompositions, where ethylene is by far the predominant neutral fragment lost, followed by $CH_3^{\cdot}$; this is consistent with the metastable spectra of similar isomers such as 2,3-dimethyl-1-pentene, 2,4-dimethyl-1-pentene and 2-methyl-1-hexene [13]. Three reactions were studied in detail: loss of $CH_3^{\cdot}$ (*m/z* 83), loss of C_2H_4 (*m/z* 70) and loss of $C_3H_5^{\cdot}$ (*m/z* 57) from the molecular ion. Some data for decomposition in the source yielding loss of C_3H_6 (*m/z* 56) and loss of the elements of $C_3H_7^{\cdot}$ (*m/z* 55) are also reported.

The set of used labeled compounds furnish us with more data than needed to calculate the probability for the loss of a given position to the neutral fragment. Therefore we made use of a least squares treatment of the data [18] to get the maximum of

Table 1. *Spectra of 4,4-Dimethyl-1-pentene in % of the Total Ion Current*

Type of spectra		Source		MIKE
Ionizing energy		70 eV	10 eV	70 eV
Fragment lost	*m/z*			
(*M*)	98	0.5	13.2	–
$H^{\cdot}$	97			
$CH_3^{\cdot}$	83	5.4	4.2	12.5
CH_4	82	0.2	0.2	0.5
C_2H_4	70	1.0	13.1	79.0
$C_2H_5^{\cdot}$	69	0.2		1.1
C_2H_6	68	0.1		0.3
$C_2H_7^{\cdot}$	67	0.6		
$C_3H_5^{\cdot}$	57	41.3	67.5	4.5[a]
C_3H_6	56	2.3	1.5	1.9
$C_3H_7^{\cdot}$	55	11.2	0.3	0.2
C_3H_8	54	0.2		
$C_3H_9^{\cdot}$	53	0.8		
$C_4H_7^{\cdot}$	43	1.5		
C_4H_8	42	0.9		
$C_4H_9^{\cdot}$	41	15.6		
C_4H_{10}	40	0.8		
$C_4H_{11}^{\cdot}$	39	4.7		
$C_5H_9^{\cdot}$	29	8.9		
C_5H_{10}	28	1.1		
$C_5H_{11}^{\cdot}$	27	2.7		

[a] The distribution of the ions containing four C-atoms depends on the temperature of the inlet system.

Table 2. *Probability (%) of the Loss of the Label to the Neutral Fragment in 4,4-Dimethyl-1-pentene*

Position of the label	$CH_3^{\cdot}$ Source	MIKE	C_2H_4 Source	MIKE	$C_3H_5^{\cdot}$ Source[b])	C_3H_6 Source	$C_3H_7^{\cdot}$ Source
1	4	15	55	50	99	100	32
2	0	1	14	21	98	100	29
3	0	9	50	50	98	98	32
4	0	1	0	2	0	0	33
5	32	25	25	23.4	0	0	57
1,2	1		55 (0)[c])	(11)	0 (100)	0 (97)	30 (10)
1,3	3		86 (13)	(6)	0 (98)	0 (97)	60 (19)
1,4	3		62 (0)	(1)	99 (1)	100 (0)	72 (15)
1,5	33		61 (11)	(11)	98 (2)	100 (0)	67 (12)
2,3	0		50 (9)	(11)	2 (96)	0 (100)	37 (16)
[a])	95	101	194	193	296	299	297
est. error	±2	±1	±2	±1	±2	±5	±5

[a]) Sum of losses from singly labeled species (theoretical value without isotope effect: n · 100, where n is the number of C-atoms lost).

[b]) The results for the metastable data were not evaluated separately. See *Table 3*.

[c]) The probability for the loss of two labeled atoms is given in parenthesis.

information. The values given in *Table 3* result from such calculations. The standard deviation for the results accounting for decomposition within the source is 1–2% and decreases to values lower than 0.5% for metastable decay data. Thus the standard error of the calculated relative contributions is very small. However, the computed data are somewhat biased by the fact that not all positions have the same statistical weight. We indicate on the bottom of *Table 2* an error that we consider to be a conservative estimate.

Table 3. *Relative Participation (%) of Different Reaction Paths in 4,4-Dimethyl-1-pentene*

$-CH_3^{\cdot}$ Position	1		3	5	
Source	4			3 × 31	
Metastable	16		9	3 × 25	
$-C_2H_4$ Positions	$1\cap2$	$1\cap3$	$1\cap5$	$2\cap3$	$3\cap5$
Source	5	10	3 × 14	8	3 × 11
Metastable	11.1	6.0	3 × 11.8	10.6	3 × 11.9
$-C_3H_5^{\cdot}$ Positions	$1\cap2\cap3$	$1\cap2\cap5$	$1\cap3\cap5$	$2\cap3\cap5$	
Source	100				
Metastable	73	3 × 4	3 × 2	3 × 3	
$-C_3H_6$ Positions	$1\cap2\cap3$	$1\cap2\cap5$	$1\cap3\cap5$	$2\cap3\cap5$	
Source	100				
Metastable	22	3 × 10	3 × 10	3 × 6	

Loss of CH_3. The results given in *Table 3* show that the vast majority (93%) of the methyl loss within the ion source comes from positions 5,5′ and 5″, *i.e.* the three methyl groups (as would be expected), plus a small contribution of C-1. C(1) becomes substantial in the metastable time range (16%), where C(3) accounts for 9%, thus indicating a partial skeletal rearrangement. It may be mentioned that the loss of an internal position as CH_3 forms a large proportion of the methyl loss within the source for 1-hexene, 1-heptene and 1-nonene and becomes a major part in their metastable decomposition [4] [5] [9]. It is interesting to compare 4,4-dimethyl-1-pentene with 5-methyl-1-hexene [20], where in the metastable time range, position 4, *i.e.* the position *a* of the longest chain to the most substituted C-atom, is lost with the same probability as position 1 (18%) and the other positions of the chain are not eliminated at all.

Further decomposition of the resulting $C_6H_{11}^+$ $(M-CH_3)^+$-ions was also studied in the metastable region. These ions fragment almost exclusively by further loss of C_2H_4 to give $C_4H_7^+$. The ion current due to this reaction accounts for 99% of the total fragment ion current due to decomposition of $C_6H_{11}^+$. By choosing to look at the decay of only $^{13}CC_5H_{11}^+$- and $^{13}C_2C_4H_{11}^+$-ions formed from singly and doubly labeled molecular ions, respectively, we could study a set of fragment ions presumably labeled in different positions. As *Table 4* shows, all the $(M-CH_3)^+$-ions behave in essentially the same way, regardless of the original label position. Loss of two C-atoms at random from singly labeled $C_6H_{11}^+$ would give 33% loss of label, while for random loss from the doubly labeled species the calculated values are 53% for the loss of one C and 7% for loss of both. All the values in *Table 4* agree with these values within experimental error. Thus all C-atoms become completely equivalent at least in those alkenyl ions that lose C_2H_4 and no information about their original structures can be gleaned. C-randomization in other alkenyl ions has been reported previously [21].

Loss of C_2H_4. The origin of the atoms lost from alkenes as C_2H_4 is not straightforward [3–10] [22] and the present results are not exceptional in this regard as is shown by the data of *Table 3*. However, they represent to our knowledge the first case where the available doubly labeled compounds furnish all combinations of the two positions lost to the neutral fragment and demonstrate a most peculiar behavior: the

Table 4. *Percentage Loss of Label from* ^{13}C*-Labeled* $C_6H_{11}^+$ *in the Reaction* $C_6H_{11}^+ \rightarrow C_4H_7^+ + C_2H_4$

Labeled position	Loss [%]	Labeled[a] positions	Loss [%]	
1	35	1,2	(−1)[b]	52
2	30		(−2)	1
3	33	1,3	(−1)	54
4	32		(−2)	6
5	34	1,4	(−1)	53
			(−2)	5
		1,5	(−1)	53
			(−2)	7

[a] Refers to labeled position in the precursor molecule.

[b] The figures preceeded by (−1) are the loss of $^{13}C_1$, (−2) of $^{13}C_2$.

eight combinations $C((1\cap 3)'\cap(2\cap 5\cap 5'\cap 5'')')$, *i.e.* either position 1 or 3 with any of the positions 2 or 5, participate all equally within one percent to the metastable decay. $p(1\cap 3) = 5.6$ is calculated to be half of the corresponding value of such a combination. Positions 2,5,5′ and 5″ become equivalent and are never lost simultaneously to C_2H_4. Each of those are lost with either position 1 or position 3 which participate with the same probability (50%) to C_2H_4 loss. Position 4 is never lost in this decomposition. Therefore one must assume a rearrangement of long-lived 4,4-dimethyl-1-pentene molecular ions to a structure or mixture of structures for which the mechanism of C_2H_4 loss allow distinction between 3 sorts of C-atoms.

It is easy to understand that the data for the decomposition within the ion source are even harder to interpret since they represent a time average over reactions occurring between 10 ps and 2 μs.

The subsequent behavior of the $C_5H_{10}^{+}$-ions formed by loss of ethylene from the molecular ion was also studied in the metastable region. The two most important decompositions of $C_5H_{10}^{+}$-ions are loss of CH_3 to yield $C_4H_7^+$ (*m/z* 55) and loss of C_2H_4 to give $C_3H_6^{+}$ (*m/z* 42). They provide about 50% and 25%, respectively, of the total metastable fragment ion current. The decay of three labeled $C_5H_{10}^{+}$-ions, namely those formed by loss of $^{12}C_2H_4$ from molecular ions labeled at C-3, C-4 and C-5 was studied. Again, as in the case of the fragmentation of secondary $C_6H_{11}^{+}$-ions, the percent of ^{13}C loss from these ions in either of the two fragmentations studied was within experimental error as calculated for a random distribution. This result is in agreement with previous data on ^{13}C-labeled $C_5H_{10}^{+}$-ions formed from 2-methyl-1-hexene [11], and is consistent with metastable decomposition results for other $C_5H_{10}^{+}$-ions [23].

The measurement of the metastable peak width enabled us to calculate the release of translational kinetic energy (T) in the loss of C_2H_4 from the molecular ion [24]. All possible isotopic combinations from all labeled compounds were measured at least three times and the data again subjected to a least squares treatment whose result is presented in *Table 5*. $C((1\cap 3)'\cap 5)$ has the smallest 0.97 kJ/mol and $C((1\cap 3)'\cap 2)$ the

Table 5. *Release of Translational Energy in the Loss of C_2H_4 from 4,4-Dimethyl-1-pentene Ion*

Reaction	T [kJ/mol]
$C(1\cap 5)$	0.97
$C(3\cap 5)$	1.00
$C((1\cap 3)'\cap 5)$	0.95
$C(1\cap 2)$	1.26
$C(3\cap 2)$	1.14
$C((1\cap 3)'\cap 2)$	1.25
$C(1\cap 3)$	1.06
Average value[a])	1.09
Unlabeled compound[b])	1.14
Standard deviation[c])	0.015
Standard error	0.004

[a]) Of all labeled compounds.

[b]) Average of several measurements.

[c]) From least-squares treatment results.

largest (1.22 kJ/mol) value. The differences seem statistically significant, but since we do not know of any comparable investigations we think it premature to draw any mechanistic conclusions from these results.

The dependence of the fragmentation upon the energy of the ionizing electrons was also measured. The probability of the different positions lost in a neutral fragment containing one or three C-atoms within the source does not change. However, this is not the case for the loss of ethylene: below an energy of (nominally) 16 eV the probability p $((1 \cap 3)' \cap 2)$ gradually diminishes to zero near the appearance potential with a corresponding increase of the probabilities for the other positions. This behavior should be compared with the slightly higher T-values for the elimination of the position 2 (see *above*), indicating a somewhat higher activation energy for fragmentation involving this position.

Loss of C_3-Fragments. The spectrum of 4,4-dimethyl-1-pentene contains peaks at *m/z* 57, 56 and 55, corresponding to loss of $C_3H_5^{\cdot}$, C_3H_6 and $C_3H_7^{\cdot}$, respectively, but only the transitions $98^+ \rightarrow 57^+$ and $98^+ \rightarrow 56^+$ are intense in the metastable region (see *Table 1*). The results of the least-squares calculations are given in *Table 3*. $C_3H_5^{\cdot}$-loss proceeds exclusively by an allylic cleavage. The same is true for the loss of C_3H_6 occurring within the ion source, where the expected *McLafferty* rearrangement almost certainly involves a transfer of one of the primary H-atoms of positions 5, 5′ or 5″. This mechanism accounts only for 22% of this fragmentation in the metastable range; the data give evidence for other structures that the limited number of labeled compounds do not allow to determine unambiguously.

Loss of C_3H_7 very probably occurs in two steps: consecutive loss of $CH_3^{\cdot}$ and C_2H_4. This is the reason why this reaction is too weak in the metastable decay to be treated quantitatively. To determine the sequence in which these two losses occur, the expected retention of ^{13}C in the $C_4H_9^+$-ion can be calculated from the data of *Table 3* by assuming that the subsequent decay of $C_6H_{11}^+$- or $C_5H_{10}^{+\cdot}$-ions occur in a random fashion. The calculated figures given in *Table 6* are to be compared with the corresponding figures in the last column of *Table 2* and point clearly to loss of $CH_3^{\cdot}$ followed by loss of C_2H_4 as the major process, with at most a minor contribution from the competing process. The data are fully explicable without any skeletal rearrangement of the molecular ion.

Table 6. *Calculated Percent Retention of ^{13}C in $C_4H_9^+$-Ions Following Loss of $CH_3^{\cdot}$ and C_2H_4*

Labeled position	Loss of $CH_3^{\cdot}$, then C_2H_4	Loss of C_2H_4, then $CH_3^{\cdot}$
1	36	68
2	33	36
3	33	52
4	33	20
5	54	42

Discussion. – Little is known about the mechanistic details of the various processes responsible for ethylene (and propylene) loss. Loss of C-3 and C-5 together from 2,4-dimethyl-1-pentene was suggested by *Stefani* [23] based on results with deuterium labeling. Reaction analogous to C$(1 \cap 5)$ for the elimination of ethylene have not previously been reported. The data for ethylene loss from linear alkenes with 6 to 14 C-atoms that are under study in this laboratory show very different behavior; the ethylene lost in the metastable fragmentation comes mainly from the innermost positions and involves always two neighbouring C-atoms [19]. If these alkenes rearrange, they do it definitely not go to a branched structure.

Some further insight can be gained when the results are viewed from a thermodynamic standpoint. It is usually assumed that ions fragmenting in the metastable region possess less internal energy than those decomposing within the source *i.e.* the equivalent rovibronic temperature of the former is lower and thus the importance of the activation entropy is less. This is equivalent of saying that the competition between different reaction paths is, in the metastable region, mainly governed by differences in the activation energy. According to *Bowen & Williams* [24], loss of C_2H_4 and CH_3 are the lowest energy unimolecular decomposition processes available for the observed reactions, assuming the most stable product configurations (see *Table 1*). The relative importance of the various modes of C_2H_4-loss changes only moderately with internal energy. The data in *Table 2* show some differences between source and metastable data, but they are minor compared to the overall shifts in importance of C_2H_4- and C_3H_5-loss as seen in *Table 1*. The relative metastable intensity of the latter reaction is roughly 20% of that for C_2H_4-loss, which is presumably attributable to the fact that it is 25 kJ/mol [24] more expensive in energy than C_2H_4-loss. This would imply that the range of activation energies of various parallel reaction channels for the latter loss must be somewhat less than 25 kJ/mol in order to account for the lack of drastic shifts in going from the source to metastable decompositions. This is especially true since it is unlikely for the allylic cleavage to possess a very high entropy factor. Beside the relative intensity differences, the main differences between the data from the source and metastable decompositions is the increasing equivalence of C-1 and C-3 with time, as seen from the C_2H_4- and the CH_3-losses. Both positions are equivalent for the allylic cleavage, thus we cannot distinguish between different isomeric precursors for these reactions. Further studies of the energetics of these reactions are in progress.

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