

79. The Mass Spectrometric Fragmentation of 1-Alkyl Ions derived from Halides

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Summary. The mass-spectrometric fragmentation of *n*-pentyl, *n*-hexyl, *n*-octyl and *n*-nonyl ions has been studied using ^{13}C - and D-labelling. The ions were produced from the corresponding halide ions. The loss of an olefin as a neutral fragment is the main reaction. The elimination of this fragment must be by a complex mechanism, since the terminal carbon atoms have the smallest probability of being lost with the neutral fragment. On chains with five to six carbon atoms, hydrogen scrambling seems to precede the fragmentation; this is not true for hydrogen on terminal positions of longer chains. Ring formation prior to the fragmentation could explain some of the results; but no reasonable conclusion could be reached.

1. Introduction. – In two preceding publications [1] [2] we described the measurement of the fragmentation of butyl and *n*-heptyl ions formed from the corresponding halides. For butyl ions we postulated the formation of a protonated four-membered ring as an intermediate in order to explain the equivalence of the carbon atoms in the elimination reaction of ethylene. We were able to show that every carbon atom in the heptyl ion has a well defined probability of loss as either ethylene or propene; in contrast to butyl ions, this probability is position dependent. However we were unable to conceive a model which would explain the observed results. Whereas with butyl ions there seems to be a scrambling of the hydrogen atoms that finally leads to a statistical distribution without any noticeable isotope effect for hydrogen and deuterium, this is not the case for the fragmentation of heptyl ions. Some hydrogen rearrangement can be detected but a statistical partition among the different positions within the molecule has not been observed. This has also been reported for the decomposition of decyl ions produced by chemical ionization [3].

In the course of the chemical synthesis of ^{13}C - or D-labelled heptyl halides, some halides with five to nine carbon atoms appeared as intermediate products or were easily obtainable from a product with seven carbon atoms. We examined the mass spectrometric fragmentation of these products in order to confirm the reactions we had found for the parent ions with four and seven carbon atoms. Notwithstanding the fact that the labelling of the products with five to nine carbon atoms is not as complete as it was for the heptyl halides, we think that we can draw some conclusions worth communicating.

2. Experimental. – The synthesis and experimental conditions were the same as those described in the previous publication [2]. A double focussing mass spectrometer was used with a source temperature of 120° and an electron energy of 70 eV. The defocussing technique was applied in order to study the metastable reactions. The following labelled products were synthesized:

1-C ₅ H ₁₁ I:	1- ¹³ CD ₂ ; 2- ¹³ CD ₂ ; 3- ¹³ C; 5- ¹³ C; 1,5- ¹³ C ₂ ; 1,2- ¹³ C ₂ .
1-C ₅ H ₁₁ Br:	1- ¹³ CD ₂ ; 1,5- ¹³ C ₂ .
1-C ₆ H ₁₃ I:	1- ¹³ C; 3- ¹³ C; 6- ¹³ C; 1,5- ¹³ C ₂ ; 1,6- ¹³ C ₂ .
1-C ₆ H ₁₃ Br:	1- ¹³ C; 3- ¹³ C; 1,5- ¹³ C ₂ .
1-C ₈ H ₁₇ I:	1- ¹³ C; 3- ¹³ C; 5- ¹³ C; 7- ¹³ C ₁₃ ; 1,7- ¹³ C ₂ ; 2,8- ¹³ C ₂ ; 1,3- ¹³ C ₂ ; 3,7- ¹³ C ₂ .
1-C ₈ H ₁₇ Br:	1- ¹³ C; 7- ¹³ C; 1,3- ¹³ C ₂ .
1-C ₉ H ₁₉ I:	1- ¹³ C; 2- ¹³ C; 5- ¹³ CD ₂ ; 8- ¹³ C; 1,2- ¹³ C ₂ .
1-C ₉ H ₁₉ Br:	5- ¹³ CD ₂ .

3. Ions containing halogen. – The main reactions of the molecular ions are the loss of halogen and of hydrogen halide as neutral fragments. The former reaction is by far the most important, especially for the iodides, thus conveniently allowing the study of the fragmentation of the corresponding alkyl ions. The loss of HI represents less than 2% of the alkyl formation for iodides, the loss of HBr from the bromides is between 5 and 50%. A small amount of the fragments of the general formula C_mH_{2m}X⁺ from the parent compound C_nH_{2n+1}X⁺ (m < n) seems to be due to a simple C–C bond scission with the loss of an alkyl radical as a neutral fragment. However, for the bromides (and chlorides) with n ≥ 6, the ion C₄H₈Br⁺ is of some importance. This ion is especially apparent for n ≥ 8, where it forms the base ion. The direct formation of the ion C₄H₈Br⁺ (and sometimes C₅H₁₀Br⁺) from the molecular ion can also be observed as a metastable transition. *Mac Lafferty* has explained its stability by ring formation [4]:



The ions labelled with ¹³C or D show that there is practically no exchange between the atoms of the alkyl group R and the ring. This is confirmed by the metastable decompositions which indicate that at least 97% of the ions show no exchange reaction before fragmentation. The stability of the five-membered ring ion is supported by the fact that we are unable to find any metastable reaction originating from this ion. The ion C₂H₄Br⁺ (8% of C₄H₈Br⁺) mainly emanates from the molecular ion directly by fast reactions, the formation from C₄H₈Br⁺ by loss of ethylene being negligible. The findings for C₅H₁₀Br⁺ are similar, so a six-membered ring structure may be assumed.

It may be mentioned that the ion C₂H₄I⁺ appears to result from a simple bond scission between the carbon atoms C(2) and C(3). Some hydrogen rearrangement can be observed however (about 16% from position 3, 9% from position 4 and 5% from position 5 for 1-heptyl iodide). Furthermore this ion contains a contribution of 5% of carbon atoms from position 3 and 4% from position 4 (for 1-heptyl iodide). These contributions, however small, show the complexity of formation of this (unimportant) ion.

4. Pentyl ion. – The mass-spectra of the 1-pentyl iodides are presented in Table 1. Only fragments not containing halogen are given, they have not been corrected for incomplete deuteration or for ¹³C enrichment. At the top of each column the degree

of deuteration or enrichment in ^{13}C are given. The figures are normalized to the 'parent' ion $(M - I)^+ \equiv 100$. In Table 2 we give a simplified fragmentation scheme, normalized to the sum of the alkyl fragments shown. It can be seen that the loss of ethylene is the main fragmentation reaction in the source and practically the only reaction that can be observed in the (slow) metastable decay.

Table 1. *Low-resolution mass-spectra of 1-pentyl iodide labelled with D and/or ^{13}C . Uncorrected spectra. Only fragments without halogen are given*

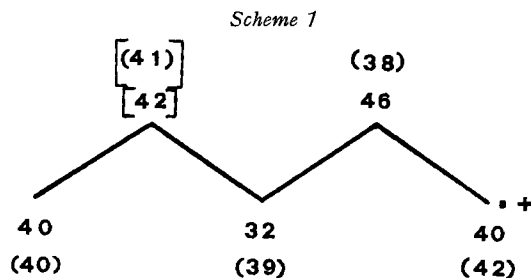
Mass unlabelled	1-D ₂	1- ¹³ CD ₂	2- ¹³ CD ₂	3-D ₂	1,3-D ₄	3- ¹³ C	4-D ₂	5-D ₃	5- ¹³ C	1,5- ¹³ C ₂	1,2- ¹³ C ₂
	¹⁸ C ₂ C ₃ H ₁₁ I ⁺										38.8
¹³ CC ₄ H ₁₁ I ⁺	98.7*	64.1	56.0	99.1*	99.3*	64.5	98.8*	99.2*	56.7	46.8	47.2
C ₅ H ₁₁ I ⁺		35.9	44.0			35.5			43.3	14.4	15.8
$\Sigma(M - I)^+$	$\equiv 100$	$\equiv 100$	$\equiv 100$	$\equiv 100$	$\equiv 100$	$\equiv 100$	$\equiv 100$	$\equiv 100$	$\equiv 100$	$\equiv 100$	$\equiv 100$
59						6.2					
58		6.5	6.7			9.3		9.1			
57		13.8	7.4	11.9	10.7	8.1		35.5	6.9	3.8	6.2
56	0,2	7.3	3.9	8.0	11.1	4.9	14.4	15.1	3.8	15.5	12.8
55	52	7.3	6.2	4.5	3.8	2.3	12.9	19.6	9.4	26.7	7.1
54	2	1.4	1.1	2.4	2.3	1.6	2.8	3.7	1.5	4.3	2.6
53	8.6	2.4	1.4	2.0	1.5	1.3	2.3	3.8	2.3	6.0	2.0
47						31					
46			35	28		106		66			
45		93	78	97	89	109		54	98	21	25
44		108	79	109	122	56	90	75	70	103	101
43	409	69	46	62	59	40	143	52	32	197	84
42	41	34	23	42	30	33	55	41	23	63	50
41	131	38	31	52	17	28	41	49	38	101	31
40	9	17	8	23	17	22	29	21	13	25	24
39	58	21	14	29	8	8	22	38	25	60	18
33						2					
32			6	6		11		27			
31		13	11	20	5	15		22	8	0.3	5
30		19	14	33	15	30	7	18	11	26	26
29	65	39	34	56	20	50	54	24	35	64	28
28	16	19	30	28	17	30	27	36	25	44	31
27	69	35	26	54	20	29	53	41	35	80	30

* % of deuteration.

Table 2. *Fragmentation scheme for C₅H₁₁⁺ in % of the fragments*

	C ₅ H ₁₀ ⁺	C ₅ H ₉ ⁺	C ₄ H ₈ ⁺	C ₄ H ₇ ⁺	C ₃ H ₇	C ₃ H ₆ ⁺	C ₃ H ₅ ⁺
source	0.1	0.4	0.1	8.1	63	6.3	21
metastable	0.1	0.1	0.1	0.6	98	0.4	0.5

Since we have labelled four different positions of the molecule with ^{13}C , we can estimate the probability of each position being lost with the neutral ethylene fragment. We obtain the following values:



The values given in parenthesis are for the metastable decay, those in brackets were estimated by taking the difference to 200%. The average error is estimated to be 1% except for position 2, where it is possibly somewhat larger because this position contained simultaneously ^{13}C and D_2 . The figures leading to this distribution are given in Table 3, together with the values calculated for complete randomisation. For fast decay within the source there is a definite probability that each position may be lost as ethylene, including the central position. Again it can be seen that direct fragmentation is not the only process leading to the elimination of ethylene. For metastable decay, all carbon atoms have the same probability within the limits of error.

The distribution of deuterium in the fragments is given in Tables 3 & 4. For the slow metastable decay, a statistical distribution of the D-atoms within the 'parent'

Table 3. Elimination of ethylene from $\text{C}_6\text{H}_{11}^+$ labelled with ^{13}C and D in %

Fragment lost	Source				Metastable				stat. exp.	
	1- $^{13}\text{C}\text{D}_2$	2- $^{13}\text{C}\text{D}_2$	3- ^{13}C	5- ^{13}C	1- $^{13}\text{C}\text{D}_2$	2- $^{13}\text{C}\text{D}_2$	3- ^{13}C	5- ^{13}C	0D	2D
C_2H_4	30	22	68	60	23	24	61	60	60	22.9
$\text{C}_2\text{H}_3\text{D}$	26	26			29	32				30.5
$\text{C}_2\text{H}_2\text{D}_2$	4	6			6	6				6.5
$^{13}\text{CCH}_4$	10	16	32	40	17	14	39	40	40	15.3
$^{13}\text{CCH}_3\text{D}$	20	19			21	20				20.4
$^{13}\text{CCH}_2\text{D}_2$	10	11			4	4				4.4

Table 4. Elimination of ethylene from $\text{C}_6\text{H}_{11}^+$ labelled D in %

Fragment lost	Source				Metastable				stat. exp.		
	5- D_3	3- D_2	1,3- D_4	1- D_2	5- D_3	3- D_2	1,3- D_4	1- D_2	2D	3D	4D
C_2H_4	31	46	12	40	23	40	14	40	38.2	21.2	10.6
$\text{C}_2\text{H}_3\text{D}$	39	46	41	47	51	52	43	50	50.9	50.9	42.4
$\text{C}_2\text{H}_2\text{D}_2$	26	8	38	13	24	8	34	10	10.9	25.5	38.2
C_2HD_3	4		8		2		8			2.4	8.5
C_2D_4			1				0				0.3

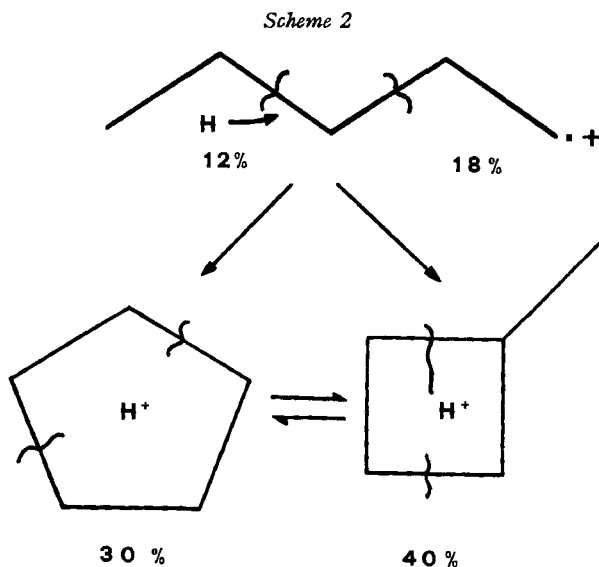
ion is observed. This is not quite true for the fast decay within the source. It can clearly be seen that there must be some scrambling before fragmentation occurs. This is most visible for the samples that were labelled simultaneously with ^{13}C and D (Table 3) and for the metastable decay there seems to be very little correlation between the loss of deuterium and that of carbon atoms in the same position. The decay seems to be similar to the fragmentation of butyl ions [1].

The results for molecules with two carbon atoms simultaneously labelled are given in Table 5. There are several possibilities to obtain a calculated distribution: Firstly

Table 5. Elimination of ethylene from $\text{C}_5\text{H}_{11}^+$ doubly labelled with ^{13}C

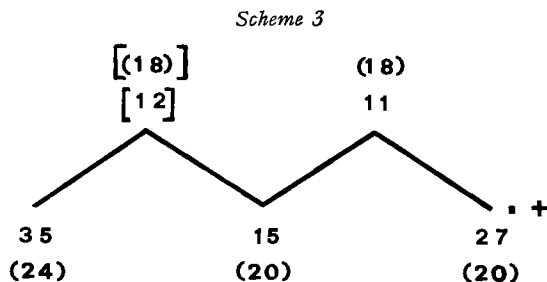
Fragment lost	Source				Metastable				Calculated	
	$1,2-^{13}\text{C}_2$		$1,5-^{13}\text{C}_2$		$1,2-^{13}\text{C}_2$		$1,5-^{13}\text{C}_2$		random	5-ring
	meas.	calc.	meas.	calc.	meas.	calc.	meas.	calc.		
C_2H_4	32	32.4	30	36.0	32	36.0	31	34.8	30	40
$^{13}\text{CCH}_4$	50	49.2	60	48.0	57	48.0	56	48.4	60	40
$^{13}\text{C}_2\text{H}_4$	18	18.4	10	16.0	11	16.0	13	16.8	10	20

we can use the measured probability for the two positions and calculate the distribution on the assumption that both positions are lost independently; these figures are given under the heading 'calc.'. Secondly, we can assume that a five-membered ring is formed and that ethylene is eliminated as two consecutive carbon atoms of the parent ion. Thirdly, we can compute the chance of losing any two carbon atoms at random. This last possibility fits best the results for metastable fragmentation. As in the case of heptyl ions [2], we may again assume three intermediate states, *viz.* direct fragmentation, a protonated cyclopentane and a protonated methylcyclobutane as follows:



An equilibrium between the five and the four-membered rings must also be assumed in order to explain the randomisation observed for the metastable fragmentation. The contribution of the different structures are found by trial and error. The following are the probabilities for the different positions (from pos. 1 to 5): 40%, 50%, 32%, 44%, 34%.

The loss of methane from pentyl ion is a minor reaction, however it can conveniently be studied. The probability for a particular position to be lost is given by the following diagram:



Every position has a definite chance to be lost as methane, but in the fragmentation in the source, the terminal positions are favoured. This can also be seen from the distribution of the deuterium given in Table 6. The carbon atoms are equivalent for the slow metastable decay, but the deuterium atoms are not yet completely randomised. This might be explained by an exchange *via* the additional proton of the ring

Table 6. Elimination of methane from $C_5H_{11}^+$

Fragment lost	Source				Metastable				Statist.				
	5-D ₃	3-D ₂	1-D ₂	1,3-D ₄	5-D ₃	3-D ₂	1-D ₂	1,3-D ₄	2D	3D	4D		
				meas.				calc.				meas.	calc.
CH ₄	35	46	49	24	22.5	35	40	42	18	16.8	38.2	21.2	10.6
CH ₃ D	20	46	28	33	35.5	36	48	43	38	37.3	50.8	50.9	42.4
CH ₂ D ₂	12	8	23	28	27.4	19	12	15	34	31.7	11.0	25.5	38.2
CHD ₃	32			14	12.8	10			10	12.4		2.4	8.5
CD ₄				1	1.8				0	1.8			0.3

structures, as we have assumed for butyl ion. The loss of methane is inherently more sensitive to complete randomisation than is that of ethylene. If we assume the same reaction scheme for the loss of methane as we did above for ethylene, we obtain the following distributions (from pos. 5 to 1): 34%, 9%, 13%, 9%, 37%. We supposed that there is a 50% chance to form the methane from the methyl group of the protonated methylcyclobutane. This corresponds to the value observed for methylcyclopentane ions [5]. The aspect of the distribution is reproduced, but without a more detailed analysis of the decay of protonated rings, our model remains purely hypothetical.

5. Hexyl ion. – In contrast to pentyl ions, hexyl ions lose only negligible amounts of methane as neutral fragments, the elimination of ethylene and propene being the

main reactions aside from the apparent loss of ethane and propane which may correspond to a successive elimination of olefin and H₂ (Tables 7 and 8). Only three positions have been labelled with ¹³C. The probabilities for losing an olefin with these carbon atoms are the following: (in parenthesis for metastable decay):

ethylene	1:36 (31)	3:33 (36)	6:34 (32)	stat. 33.3
propene	1:49 (50)	3:51 (52)	6:43 (50)	stat. 50

Table 7. *Low-resolution mass-spectra of 1-hexyl iodide labelled with D or ¹³C. Uncorrected spectra. Only fragments without halogen are given*

Mass	Unlabelled	1-D ₂	1- ¹³ C	3- ¹³ C	6- ¹³ C	1,5- ¹³ C ₂	1,6- ¹³ C ₂	1,6-D ₅
¹³ C ₂ C ₄ H ₁₃ I ⁺						38.2	37.8	
¹³ CC ₅ H ₁₃ I ⁺			57.4	58.7	57.3	47.1	47.2	
C ₆ H ₁₃ I ⁺		98.9*	42.6	41.3	42.7	14.7	15.0	99.5*
Σ(M-1) ⁺	≡ 100	≡ 100	≡ 100	≡ 100	≡ 100	≡ 100	≡ 100	≡ 100
74								0.4
73								0.3
72								0.6
71	0.4	1.8				2.7	0.2	1.2
70	0.2	0.6	1.3	1.5	1.8	3.7	2.1	0.4
69	2.7	0.9	1.3	1.5	3.4	1.8	1.1	0.6
62								5
61								10
60								15
59		22				4	4	11
58		20	13	12	13	18	17	9
57	34	33	26	22	25	18	18	8
56	8.5	11	16	13	14	17	19	4
55	26.5	15	17	11	20	11	13	4
48								25
47								37
46								103
45		205				13	20	93
44		153	100	69	76	131	143	46
43	276	226	240	177	155	128	136	49
42	13	53	30	29	33	49	55	23
41	99	113	77	46	61	41	53	20
40	6.3	29	14	11	10	21	22	15
39	45	47	31	14	27	17	25	11
32								16
31		22				-	-	15
30		40	7	7	9	20	24	19
29	64	114	59	33	26	34	42	26

* % of deuteration.

Table 8. *Fragmentation scheme for C₆H₁₃⁺ in % of the fragments*

	C ₆ H ₁₁ ⁺	C ₅ H ₉ ⁺	C ₄ H ₇ ⁺	C ₄ H ₆ ⁺	C ₄ H ₇ ⁺	C ₃ H ₇ ⁺	C ₃ H ₆ ⁺	C ₃ H ₅ ⁺
Source	0.2	0.6	7.4	1.8	6.0	60	2.9	21
Metastable	0.1	0.1	39	0.9	0.1	60	0.1	0.6

The figures compare rather well to a statistical expectancy for a random loss (with the exception of pos. 6 for propane). The experiments with two carbon labels in the molecule do not seem to confirm this view (Table 9). It should not be forgotten however that, whereas the percentage of loss of no ^{13}C is rather accurate for the doubly labelled molecules, the calculation of the fractions containing one and two labelled

Table 9. *Elimination of ethylene and propene from $^{13}\text{C}_2\text{C}_4\text{H}_{13}^+$ in %*

Fragment lost	Source			Metastable			Stat. exp. 2 ^{13}C
	1,5- $^{13}\text{C}_2$		1,6- $^{13}\text{C}_2$	1,5- $^{13}\text{C}_2$		1,6- $^{13}\text{C}_2$	
	meas.	meas.	calc.	meas.	meas.	calc.	
C_2H_4	34	37	42.2	43	42	46.9	40.0
$^{13}\text{CCH}_2$	62	56	45.6	50	53	43.2	53.3
$^{13}\text{C}_2\text{H}_4$	4	7	12.2	7	5	9.9	6.7
C_3H_6	14	18	29.1	20	19	25.0	20.0
$^{13}\text{CC}_2\text{H}_6$	68	72	49.8	62	62	50.0	60.0
$^{13}\text{C}_2\text{CH}_6$	18	10	21.1	18	19	25.0	20.0

carbon atoms is not very accurate since the enrichment factor for ^{13}C was only 60%. If the loss were random, we would obtain the probabilities given under the heading 'stat. exp.'. Under 'calc.' we give the probabilities calculated from the corresponding values for a single ^{13}C label assuming statistical independence for the different positions. The results do not seem to confirm either hypothesis.

Similar conclusions can be drawn from the distribution of deuterium in the fragments lost (Table 10). The results for the metastables correspond rather well to a complete scrambling of the D-atom. As we have shown for heptyl radicals, this is a relatively slow process, so that the distribution for the fast fragmentation is not at random. The probability for losing the carbon atom in pos. 1 is 36% and 49% for ethylene and propene resp., but only 19% and 31% of D_2 are eliminated with these

Table 10. *Elimination of ethylene and propene from 1-hexyl ion labelled with D in %*

Fragment lost	1- D_2		Stat. exp. 2D	1,6- D_5		Stat. exp. 5D
	s	m		s	m	
C_2H_4	47	47	46.2	15	11	9.8
$\text{C}_2\text{H}_3\text{D}$	34	45	46.2	32	39	39.2
$\text{C}_2\text{H}_2\text{D}_2$	19	8	7.6	42	38	39.2
C_2HD_3				9	11	11.2
C_2D_4				2	1	0.7
C_3H_6	43	28	26.9	9	2	1.6
$\text{C}_3\text{H}_5\text{D}$	26	51	53.8	13	14	16.3
$\text{C}_3\text{H}_4\text{D}_2$	31	21	19.3	37	40	40.8
$\text{C}_3\text{H}_3\text{D}_3$				31	34	32.6
$\text{C}_3\text{H}_2\text{D}_4$				9	9	8.1
C_3HD_5				1	1	0.5

s: source m: metastable

fragments resp.. These values are, however, larger than we would expect assuming complete randomisation. The results for 1,6-D₅-hexyl show that the process of elimination of propene (or ethylene), without the participation of the terminal positions, is of some importance. We might infer from these results that the fragmentation of hexyl ions is a rather complicated process, so that a complete randomisation of the carbon and hydrogen atoms takes place only after a long period.

Tatarczyk & v. Zahn studied the time dependence of the loss of propene and ethylene from *n*-paraffin ions in the time range of 5 ÷ 500 μs [6]. They state that the observed time dependence could be explained by assuming several processes. This confirms our findings without however giving us an additional means for separation of these processes.

6. Octyl ion. – The fragmentation of 1-octyl ions has only been studied for molecules labelled with ¹³C. The relevant results are given in Tables 11 and 12. The main

Table 11. *Low-resolution mass-spectra of 1-octyl iodide labelled with ¹³C.* Uncorrected spectra. Only fragments without halogen are given

Mass	Un-labelled	1- ¹³ C	3- ¹³ C	1,3-2 ¹³ C	1,7-2 ¹³ C	5- ¹³ C	7- ¹³ C	2,8- ¹³ C ₂	3,7- ¹³ C ₂
¹³ C ₂ C ₈ H ₁₇ I ⁺				34.9	35.1			32.4	38.8
¹³ CC ₇ H ₁₇ I ⁺		62.5	56.6	47.8	47.7	58.2	58.0	48.4	46.9
C ₈ H ₁₇ I ⁺		37.5	43.4	17.3	17.2	41.8	42.0	19.2	14.3
Σ(M – I) ⁺	≅ 100	≅ 100	≅ 100	≅ 100	≅ 100	≅ 100	≅ 100	≅ 100	≅ 100
87				1.1	0.9			1.1	1.6
86		2.2	1.8	3.7	5.0	3.1	2.1	4.3	4.4
85	15.4	3.7	9.9	4.5	3.8	4.5	3.4	4.4	4.5
84	4.6								
83	6.3								
73				100	76			82	62
72		242	320	338	346	234	195	375	289
71		358	702	304	264	386	389	302	218
70		21	62	26	28	24	13	39	20
69		27	70	25	21	22	24	28	12
59				102	41			57	35
58		267	389	390	448	228	198	487	324
57	752	547	1204	552	465	570	558	539	353
56	45.6	100	447	125	122	83	56	130	72
55	139	139	497	123	108	122	113	133	53
45				49	44			5	12
44		143	338	238	340	157	142	343	226
43	624	624	1827	659	464	559	480	570	327
42	67	194	924	236	293	178	129	297	173
41	336	450	1818	417	380	363	310	400	157
40	16	69	489	86	92	52	36	91	42
39	99	164	886	131	120	113	101	147	38
31				2	2			–	–
30		34	104	57	120	35	54	116	52
29	186	340	1739	318	252	206	170	272	108
28	24	118	472	120	164	67	74	155	62
27	131	258	1329	221	193	161	138	210	80

Table 12. *Fragmentation scheme for C₈H₁₇⁺ in % of fragments*

	C ₆ H ₁₃ ⁺	C ₅ H ₁₁ ⁺	C ₅ H ₁₀ ⁺	C ₅ H ₉ ⁺	C ₄ H ₉ ⁺	C ₄ H ₈ ⁺	C ₄ H ₇ ⁺	C ₃ H ₇ ⁺
Source	0.7	28	0.6	1.5	33	2.0	6.2	28
Metastable	<0.1	56	<0.1	<0.1	43	<0.1	<0.1	n.m.

processes are again the elimination of olefins, with three to five carbon atoms, as neutral fragments. Because of the limitations of our mass-spectrometer, the metastable loss of pentene could not be measured. By comparison with the analogous loss of butene from heptyl ion and pentene from nonyl ion, we think that the ion of mass 43 is mainly formed in the two steps C₈H₁₇⁺ → C₅H₁₁⁺ → C₃H₇⁺. Both reactions can be observed as metastables, so it is probably safe to state that the main primary reactions of the octyl ion are the elimination of propene and butene in about equal amounts.

Several positions have been labelled with ¹³C. The probabilities for losing a ¹³C from a defined position during the process of olefin elimination is as follows (in parenthesis for metastables):

propene	1:34 (23)	3:46 (37)	5:33 (35)	7:40 (42)	stat.: 37.5
butene	1:45 (35)	3:56 (54)	5:49 (51)	7:53 (58)	stat.: 50.0

In Table 13 we give the results for ions labelled with two carbon atoms. As in the case of heptyl ions we see that the terminal and the central positions have the smallest

Table 13. *Elimination of propene and butene from C₈H₁₆⁺ labelled with ¹³C₂*

Fragment lost	1,3- ¹³ C ₂		1,7- ¹³ C ₂		2,8- ¹³ C ₂		3,7- ¹³ C ₂		Stat. exp. ²¹³ C
	s	m	s	m	s	m	s	m	
C ₃ H ₆	41	49	32	43	36	55	28	22	35.7
¹³ CC ₂ H ₆	38	42	62	49	60	39	58	77	53.6
¹³ C ₂ CH ₆	21	9	6	8	4	6	14	1	10.7
C ₄ H ₈	30	26	15	26	19		13	17	21.4
¹³ CC ₃ H ₈	39	59	72	55	70		65	54	57.2
¹³ C ₂ C ₂ H ₈	31	15	13	19	11		22	29	21.4

s: source m: metastable

chance of being eliminated as an olefin. The probability of losing any two specified positions at the same time is the largest for the 1,3-labelling, but this figure decreases for the metastable decay, showing that a straightforward 3–4 carbon-bond scission might contribute to the fast reaction (up to 21%), but less to the slow fragmentation. It is remarkable that all doubly labelled ions with at least one label in a terminal position have, especially for the metastable decomposition, a very high probability of losing an unlabelled olefin. As we mentioned above, the figure for the unlabelled olefin is less liable to systematic error than the other two. The fact that, for propene there is a non-negligible probability for the simultaneous loss of the 3 and 7 positions as well as a non-zero probability for not losing these two positions, demonstrates the complexity of the elimination mechanisms. The same is true for butene. Contrary to

Table 14. *Low-resolution mass-spectra of 1-nonyl iodide labelled with D and/or ¹³C Uncorrected spectra.*
Only fragments without halogens are given

Mass	Unlabelled											
		1-D ₂	1,5-D ₄	3,5-D ₄	5-D ₂	5- ¹³ CD ₂	9-D ₃	1,9-D ₅	1,2- ¹³ C ₂	2- ¹³ C	8- ¹³ C	1- ¹³ C
¹³ C ₂ C ₇ H ₁₉ I ⁺									36.1			
¹³ CC ₈ H ₁₉ I ⁺					68.8				48.6	62.0	58.1	61.8
C ₉ H ₁₉ I ⁺		99.2*	99.3*	98.9*	98.7*	37.2	99.3*	99.4*	15.3	38.0	41.9	38.2
$\Sigma(M - I)^+ \cong 100$	$\cong 100$	$\cong 100$	$\cong 100$	$\cong 100$	$\cong 100$	$\cong 100$	$\cong 100$	$\cong 100$	$\cong 100$	$\cong 100$	$\cong 100$	$\cong 100$
104								0.6				
103			0.6	1.0				1.2				
102			0.8	1.3		0.3	1.3	1.4				
101		0.3	2.0	2.6	2.6	0.9	2.8	2.3				
100		1.0	1.8	2.2	2.9	2.8	2.8	2.4	0.2	0.3	0.6	0.3
99	1.5	2.6	1.7	1.7	6.2	1.9	1.3	3.7	0.9	1.4	1.0	1.6
98	1.7											
97	3.8											
90								93				
89			83	60				32				
88			102	128		69	188	73				
87		189	84	95	174	141	15	79	61			
86		38	36	28	164	97	11	16	138	114	122	115
85	365	85	9	8	52	26	84	9	125	173	201	168
84	3.0				8		5	3	4	5	5	5
83	14				8		10	3	4	5	8	5
76								109				
75			79	46				45				
74			156	178		74	284	150				
73		271	168	213	252	219	28	156	79			
72		71	110	111	378	231	29	47	222	152	161	167
71	643	198	49	34	174	97	200	48	262	310	392	296
70	21	13	19	17	38	18	15	11	22	22	22	22
69	55	20	12	15	23	11	39	15	23	25	41	27
62								54				
61			40	24				30				
60			116	111		34	239	168				
59		211	171	203	146	144	47	174	58			
58		79	203	215	361	275	59	98	175	109	136	123
57	635	294	188	166	314	208	237	130	346	330	427	324
56	66	63	85	83	161	90	55	59	90	76	80	69
55	262	96	53	51	143	87	149	67	119	114	215	112
48								-				
47			23	17				20				
46			103	103		53	200	198				
45		159	265	279	180	213	135	252	44			
44		187	343	365	486	401	128	242	200	106	197	113
43	940	535	372	360	482	440	424	270	684	551	732	538
42	108	122	174	191	221	175	124	154	154	116	195	106
41	510	266	198	209	318	313	299	170	346	272	486	255
40	31	36	76	73	52	44	37	56	46	37	57	30

* % of deuteration.

Table 14 (suite)

Mass	Un-labelled	1-D ₂	1,5-D ₄	3,5-D ₄	5-D ₂	5- ¹³ CD ₂	9-D ₃	1,9-D ₅	1,2- ¹³ C ₂	2- ¹³ C	8- ¹³ C	1- ¹³ C
39	139	87	60	68	98	113	121	78	106	82	175	74
33			1	3				—				
32			10	15		11	64	61				
31		56	67	53	26	31	35	61	8			
30		74	94	85	58	61	38	81	37	17	95	17
29	238	207	222	204	182	309	148	128	268	186	286	172
28	55	72	99	85	65	82	83	95	74	62	120	57
27	178	130	125	152	142	196	136	91	155	117	253	108

 Table 15. Fragmentation scheme for C₉H₁₉⁺ in % of the fragments

	C ₇ H ₁₅ ⁺	C ₆ H ₁₃ ⁺	C ₆ H ₁₂ ⁺	C ₆ H ₁₁ ⁺	C ₅ H ₁₁ ⁺	C ₅ H ₁₀ ⁺	C ₅ H ₉ ⁺	C ₄ H ₉ ⁺
Source	0.2	21	0.1	1.7	37	1.1	3.0	36
Metastable	<0.1	36	<0.1	<0.1	55	60.1	60.1	8

alkyl ions with less than seven carbon atoms, there is no apparent randomisation of the carbon atoms in an octyl ion.

7. Nonyl ions. — The fragmentation data for 1-nonyl ions are presented in Tables 14 and 15. The main neutral fragments lost are propene, butene and pentene. The ion C₄H₉⁺ is not only formed by a single reaction step from C₉H₁₉⁺, but also by the reaction sequence C₉H₁₉⁺ → C₆H₁₁⁺ → C₄H₉⁺ as is shown by the corresponding metastable reactions. The relatively small loss of pentene in the metastable decay seems to indicate the importance of the above-mentioned reaction sequence. Measurements to elucidate the respective contributions are under way. The probabilities for the loss of a specified position as a neutral olefin fragment are as follows (in parenthesis for the metastables):

propene	1:34 (25)	2:36 (34)	8:35 (41)	stat.: 33.3
butene	1:41 (33)	2:47 (39)	8:49 (49)	stat.: 44.4

No systematic study has been made for the elimination of pentene. The study of the decay within the source suffers from the fact that we cannot distinguish between

 Table 16. Loss of propene and butene from 1,2-¹³C₂-nonyl ion in %

Fragment lost	Source		Metastable		Stat. exp. ^{2-¹³C}
	meas.	calc.	meas.	calc.	
C ₃ H ₆	53	42.2	52	49.5	41.7
¹³ CC ₂ H ₆	34	45.6	37	42.0	50.0
¹³ C ₂ CH ₆	13	12.2	11	8.5	8.3
C ₄ H ₈	40	31.3	44	40.9	27.8
¹³ CC ₃ H ₈	32	49.4	36	46.2	55.6
¹³ C ₂ C ₂ H ₈	28	19.3	16	12.9	16.6

a loss in one or two reaction steps. The metastable peaks are rather wide because the kinetic energy of the fragments is distributed among the two fragments according to their respective mass. The results for eliminating positions 1 and 2 given in Table 16 show, once more, that direct scission of the 3-4 or 4-5 carbon bond resp. is not the main process and that no randomisation of the carbon atoms is observed. The results cannot be explained by assuming an independent loss of the positions 1 and 2 either.

The results for labelling with deuterium given in Table 17 are especially instructive if a terminal position is labelled, either all deuterium atoms of this position or none of them are lost.

Table 17. Loss of propene, butene and pentene from 1-nonyl ion labelled with D in %

Fragment lost	1-D ₂		5-D ₂		9-D ₃		1,5-D ₄		1,9-D ₅		3,5-D ₄		Stat. exp.			
	s	m	s	m	s	m	s	m	s	m	s	m	2D	3D	4D	5D
C ₃ H ₆	62	65	49	43	65	73	27	27	32	46	21	15	45.6	29.5	18.4	11.1
C ₃ H ₅ D	12	14	45	48	4	3	33	37	10	12	42	43	45.6	48.3	44.3	36.9
C ₃ H ₄ D ₂	26	21	6	9	2	2	27	24	28	21	29	33	8.8	20.1	30.2	36.9
C ₃ H ₃ D ₃					29	22	11	10	26	19	8	8		2.1	6.7	13.4
C ₃ H ₂ D ₄							2	2	4	2	1	1			0.4	1.7
C ₃ HD ₅									0	0						0
C ₄ H ₈	53	48	32	25	57	64	15	14	24	36	9	6	32.2	17.0	8.5	4.0
C ₄ H ₇ D	12	16	50	50	3	3	33	37	10	10	29	30	51.4	45.4	34.1	22.7
C ₄ H ₆ D ₂	35	36	18	25	2	4	30	30	30	26	40	42	16.4	31.8	39.7	39.7
C ₄ H ₅ D ₃					38	29	16	14	26	21	19	19		5.8	15.9	26.5
C ₄ H ₄ D ₄							6	5	5	5	3	2			1.8	6.6
C ₄ H ₃ D ₅									5	2						0.5
C ₅ H ₁₀	45	55	21	18	48	66	8	7					21.1	8.7	3.2	
C ₅ H ₉ D	12	15	49	53	4	3	22	29					52.6	37.1	21.7	
C ₅ H ₈ D ₂	43	30	30	29	5	4	28	35					26.3	41.8	41.8	
C ₅ H ₇ D ₃					43	27	27	24						12.4	27.9	
C ₅ H ₆ D ₄							15	5							5.4	

s: source m: metastable

The results for the fast and the slow (metastable) decay differ very little, proving once again that long alkyl radicals show relatively little randomisation along the chain. The differences between the results for decay in the source and the metastable reaction are rather large for the formation of the C₄H₉⁺ ion. This is to be expected for reasons given above. The results for the metastables are not very precise, but they show that there is no randomisation in this case either.

We can summarize our results by concluding that short alkyl radical ions decay *via* one (or several) intermediate state(s) with equivalent carbon atoms, whereas the hydrogen atoms are randomised by a slower process. On increasing chain length, we can clearly distinguish between elimination reactions that involve terminal groups that show little scrambling and the loss of non-terminal carbon atoms where it is more difficult to detect an exchange of these carbon atoms. At chain lengths longer

than about six or seven carbon atoms, the randomisation of hydrogen atoms over the whole chain is unimportant but the elimination of olefins proceeds by complicated reaction steps not yet known. We thus think that, in its present state, the validity of the quasi-equilibrium theory for the prediction of the fragmentation pattern of alkyl radical ions is doubtful.

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80. Effect of Pressure in the Gamma Radiolysis of Cyclohexane in the Vapor Phase

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(3. I. 74)

Summary. The vapor phase γ -radiolysis of cyclohexane has been investigated as a function of pressure, from 100 to 0.5 Torr, in vessels of different dimensions. With decreasing pressure, the yield of hydrogen and substituted cyclohexanes is decreased and the formation of molecules having less than six carbon atoms is enhanced. The curves of yield *vs.* pressure have a sigmoid shape from which we define a transition pressure depending only on the dimensions of the vessels, the variation of the yield of a given product being the same for all the vessels. We propose and discuss a simple model of competition between the neutralization of the ions in the volume and their diffusion to the surface where they are neutralized. From the slope of the curve of the inverse of the transition pressure *vs.* the square of the characteristic diffusion length, we evaluate a maximum life-time of 68 ms for the ions, using a calculated value of the cyclohexane ions diffusion coefficient.

1. Introduction. – Several authors have explored the γ -radiolysis of cyclohexane vapor at pressures ranging from 170 to 3800 Torr and temperatures from 50° to 300°. Blachford and Dyne [1], Theard [2], Milhaud [3] [4], Sagert & Blair [5] [6], and Cosandey [7] have examined the mechanisms of reactions occurring during the radiolysis of cyclohexane vapor at a fixed pressure by means of different additives and by use of labelled compounds. Jones [8] studied this system at pressures and a temperature such that the density was as high as that of the liquid phase (300°, 0.008 to 0.42 g/cm³); with decreasing density the yield of the C₁–C₃ hydrocarbons increased by about one order of magnitude, while the yield of hydrogen and cyclohexene increased only slightly, if at all, and that of bicyclohexyl decreased by a factor of about two. The