103. Mass Spectrometric Decomposition Processes in Labelled 1-Heptenes

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Summary. The 70 eV mass spectra of a number of ^{13}C- and D-labelled analogs of 1-heptene have been measured, as well as the metastable transitions in the non-labelled compound. Isotopic distributions in the major fragment ions have been calculated from the high and low resolution data. The results show that considerable skeletal rearrangement must take place before formation of most of the fragment ions. Loss of methyl and ethyl radicals occurs mainly from the two ends of the molecule. Ethylene fragments come primarily from the unsaturated end of the molecule, but show evidence of significant prior skeletal rearrangement. The predicted *McLafferty* rearrangement accounts for only $^2/_3$ of the $C_4H_8^+$ ions formed, less for the $C_3H_6^+$ ions. At least 80% of $C_4H_9^+$ ions appear to be formed by allylic cleavage, as expected, but this mechanism can only account for a maximum of 20% of the formation of the complementary ion $C_3H_5^+$. Both, this latter ion and $C_3H_6^+$, are probably generated by loss of hydrogen from $C_3H_7^+$.

Figures obtained for label retention in 1-[^{13}C]- and 1-D-labelled analogs were nearly identical for most fragment ions, probably indicating that the hydrogen atoms in position 1 remain on C(1) even following skeletal rearrangement. A similar result was found for the 7-[^{13}C]- and 7-D-labelled compounds. The main exceptions in the case of the products labelled in position 1 ($C_4H_7^+$, $C_3H_3^+$) seem to be due to initial loss of an hydrogen atom from this position followed by further fragmentation.

1. Introduction. – The unimolecular decomposition of olefin ions was among the earliest areas to be explored by mass spectrometry, but remains one of the least well understood. Firm evidence for precise mechanisms of fragmentation is often lacking despite the nearly ubiquitous use of mass spectrometry for analysis of olefin-containing or olefin-related samples. Clearly, further elucidation of these mechanisms could be a useful aid in interpretation of spectra, but in addition, an increased knowledge of the gas phase chemistry of such relatively simple ions may offer valuable insights on a more fundamental level.

It is generally accepted that it is difficult to determine precisely the location of a double bond by means of mass spectrometry due to the considerable amount of rearrangement which may preceed decomposition [1]. The mass spectra of various D-labelled olefins confirm that intramolecular hydrogen transfer occurs prior to fragmentation [1] [2]. Several authors have invoked [1,2]- and/or [1,3]-hydrogen shifts as important pathways for these rearrangements [2]. Somewhat less attention has been paid to the possibility of skeletal isomerization in olefins, with or without concomitant hydrogen migration, although clear evidence for this phenomenon exists for some cases [3]. In the present work, we have studied the decomposition of a

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series of ^{13}C- and D-labelled 1-heptenes in order to examine the fragmentation and rearrangement processes in detail.

2. Experimental. – The low resolution mass spectra of the compounds studied were measured with a *CEC* 21-110 double focussing mass spectrometer coupled on-line to a *PDP*-12 computer [4]. Source temperature was 120° and electron energy 70 eV for all of the results presented here. Each spectrum represents an average of at least five scans. Reproducibility of intensities in individual scans was ± 2% or better for peaks larger than 5% of the total ionization and between ± 2% and ± 5% for peaks representing between 1 and 5% of the total ionization. High resolution mass spectra of the ^{13}C-labelled compounds were obtained with the same instrument. Peak multiplets were individually recorded at least ten times and the resulting intensity ratios averaged. The high resolution spectra of 1-heptene-5, 5-d_2 and 1-heptene-1, 1-d_2 were measured in the same manner with an *AEI* MS-50 mass spectrometer. Metastable transitions in the first field free region were measured by the defocussing technique [5].

The synthesis of the labelled compound has been described elsewhere [6]. Unlabelled 1-heptene (commercial product) was purified by gas chromatography. All compounds were estimated to be $\geqslant$ 99% pure, exclusive of isotopic impurities, except the 1-heptene-7-d_3. The latter compound contained a small amount of cyclohexene as impurity; only ions resulting from loss of methyl were therefore studied.

3. Results. – The uncorrected low resolution mass spectra of the compounds used in this work are given in Table 1. Intensities are given in percent of total ionization, excluding masses below 26. The isotopic compositions given were calculated from the mass spectra after correction for naturally occurring isotopes.

The distribution of ^{13}C and D in the important fragment ions of labelled 1-heptene is shown in Tables 2 and 3. The values presented in these tables were calculated from the low resolution spectra and from the individual high resolution measurements made on each relevant multiplet. When an over-determined set of equations was available, a least-squares procedure was used. Isotope effects were ignored in the calculation. The data used to calculate the results in Tables 2 and 3 were corrected in two ways. First, the contributions from unlabelled and partially labelled species were subtracted. When more than one different isotopic isomer was present as an impurity (*e.g.* 1-[^{13}C]-1-heptene and 2-[^{13}C]-1-heptene in 1,2-[^{13}C]-1-heptene, it was assumed that each possible composition of the same molecular weight contributed equally. Secondly, it was necessary to correct for the presence of naturally occurring ^{13}C. An exact correction for the natural ^{13}C in fragment ions of compounds labelled with ^{13}C cannot be made without making some assumptions about the distribution of ^{13}C in the fragment ions. However, an initial approximate calculation based on a statistical distribution of the added ^{13}C can be performed. The result of the calculation can then be used as the assumed distribution for a second successive approximation, and so on. In the present work, the residual error after the initial calculation was usually negligible compared to other uncertainties. The estimated overall uncertainty in the percentage figures in Tables 2 and 3 is ± 3, except for the figures in brackets, for which the uncertainty is ± 6.

The fragmentations which produce the results shown in Tables 2 and 3 are not straightforward. Some light is shed upon the problem by the data on metastable decompositions. Fig. 1 shows the transitions observed in the first field free region for the important ions in the mass spectrum. It should be noted that only transitions for which the daughter ion mass was equal to or greater than one half of the parent ion mass could be observed. Furthermore, the metastable pathways are not necessarily the principal processes occurring in the source. Numerous other reaction pathways not shown in Fig. 1 are suggested by studies at very high sensitivity of metastable ions in related hydrocarbons [7].

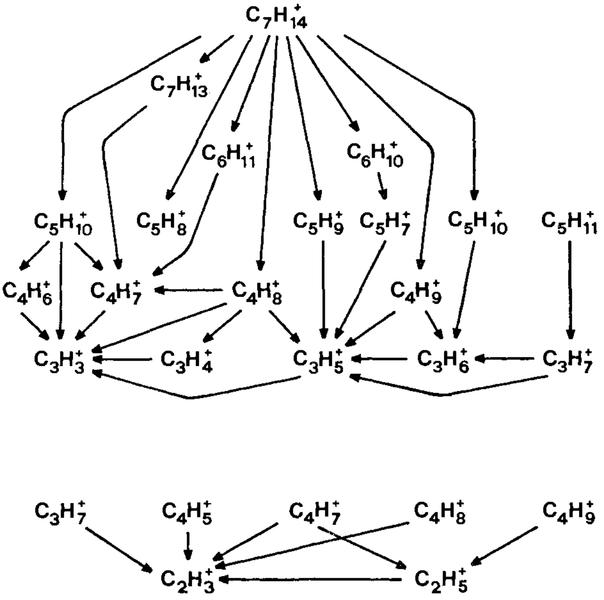


Fig. 1. *Observed metastable transitions in 1-heptene*

4. Discussion. – Perhaps the most striking feature of the results presented above is the amount of skeletal rearrangement which apparently occurs prior to fragmentation. The 'obvious' explanations of the formation of these ions, while perhaps useful, are far from representing the true situation. Even with the aid of a number of ^{13}C- and D-labelled analogs, we are unable to present an exhaustive interpretation. Nonetheless, a close examination of the results yields a number of significant and useful conclusions.

C_6 ions. – The loss of a methyl radical from the molecular ion apparently occurs to a large extent from the ends of the original molecule. About 47% of the CH_3 lost was found to contain C(7) and 28% of C(1). Of the remaining 25% which must be distributed among the other 5 carbon atoms, C(2) accounts for 12%.

The results for the compounds labelled with deuterium in positions 1 an 7 show, by comparison with those for the compounds labelled with ^{13}C in the same positions, that very little transfer of hydrogen away from these end positions occurs prior to methyl loss. In contrast, the 5,5-d_2 results indicate that the required hydrogen migration to position 1 occurs to the extent of up to 27% from position 5. Since only a maximum of 6% can come from position 7, the remaining two-thirds must come from the other four interior sites. It cannot be said with certainty whether the hydrogen transfer here is non-specific, *i.e.* occurring from several positions with similar

Table 1. *Low resolution mass spectra of 1-heptene labelled in various positions* (uncorrected spectra)

m/e	unlab.	1-[^{13}C]	2-[^{13}C]	3-[^{13}C]	7-[^{13}C]	1,2-[^{13}C]	1,3-[^{13}C]	2,3-[^{13}C]	1,2,3-[^{13}C]	1-d$_1$	1,1-d$_2$	5,5-d$_2$	7-d$_1$
103									0.01				
102						0.01	0.01	0.01	0.14		0.01	0.01	
101		0.01	0.02	0.02	0.02	0.18	0.22	0.19	3.35	0.02	0.29	0.30	0.01
100	0.02	0.19	0.29	0.24	0.29	3.36	3.98	3.32	1.06	0.32	3.95	3.93	0.28
99	0.34	2.87	4.38	3.58	4.31	0.92	0.97	0.71	0.12	3.87	0.22	0.07	3.93
98	4.41	1.74	0.49	0.59	0.57	0.08	0.05	0.01	0.01	0.15	0.01		0.18
97	0.07	0.03	0.01	0.01	0.01					0.01			0.01
87									0.02				
86						0.01	0.07	0.01	0.35		0.03	0.04	
85		0.02	0.05	0.01	0.01	0.41	0.54	0.54	0.37	0.04	0.41	0.57	0.01
84	0.05	0.36	0.63	0.62	0.46	0.33	0.38	0.20	0.08	0.46	0.06	0.23	0.38
83	0.80	0.42	0.15	0.13	0.47	0.07	0.09	0.04	0.02	0.23	0.22	0.04	0.31
82	0.02	0.02	0.04	0.02	0.01	0.01	0.01	0.01	0.04	0.04	0.03	0.01	0.04
81	0.07	0.04	0.01	0.01	0.02	0.02	0.03	0.04	0.04	0.02	0.07	0.03	0.01
80	0.01	0.03	0.04	0.03		0.01	0.01	0.01	0.05	0.04	0.03	0.03	0.10
79	0.05	0.05	0.02	0.02	0.06	0.06	0.02	0.09	0.02	0.02	0.04	0.03	0.02
78	0.03	0.05	0.08	0.06	0.03	0.03	0.01	0.01	0.01	0.04	0.04	0.04	0.09
77	0.06	0.03			0.02					0.02	0.03	0.03	0.04
74									0.02			0.01	
73						0.08	0.05	0.07	1.15		0.12	0.24	
72		0.09	0.20	0.30	0.22	1.92	1.52	1.39	3.46	0.14	2.34	4.64	0.32
71	0.38	1.95	2.69	4.47	5.48	3.11	7.23	6.07	4.76	2.70	3.37	3.94	5.33
70	6.59	6.63	6.99	5.47	3.31	4.42	3.23	2.80	2.38	5.87	3.66	2.06	2.78
69	4.78	3.30	2.39	1.36	2.86	1.93	0.88	0.83	0.50	1.88	1.76	0.64	2.55
68	0.65	0.55	0.66	0.48	0.58	0.34	0.29	0.25	0.18	0.47	0.25	0.23	0.61
67	0.48	0.28	0.25	0.16	0.35	0.23	0.21	0.23	0.08	0.19	0.18	0.12	0.46
66	0.09	0.12	0.24	0.20	0.08	0.09	0.11	0.10	0.12	0.09	0.07	0.09	0.11
65	0.21	0.10	0.08	0.04	0.17	0.13	0.15	0.12	0.08	0.07	0.07	0.06	0.22
64		0.07	0.12	0.11		0.08	0.14	0.14	0.07	0.06	0.04	0.07	0.05
63	0.16	0.10	0.12	0.06	0.02	0.07	0.07	0.03	0.03	0.09	0.09	0.07	0.16
62	0.10	0.05	0.03	0.01	0.19	0.01				0.05	0.04	0.04	0.08
61	0.01				0.02							0.03	0.02

59		0.01	0.02	0.02		0.40	0.48	0.38	3.19	0.05	0.61	2.46	0.13
58	0.18	0.51	0.82	0.66	0.10	3.78	3.98	3.61	3.55	0.88	4.54	3.93	3.09
57	4.14	6.86	8.31	7.49	3.37	6.86	7.11	6.69	5.69	7.28	6.73	10.16	8.43
56	14.45	13.99	13.37	14.07	9.19	10.40	12.23	11.57	11.80	11.16	9.67	5.08	7.78
55	9.07	7.22	6.25	4.66	9.41	5.58	3.84	3.96	3.44	5.75	5.27	3.45	5.35
54	1.37	1.39	1.55	1.58	5.88	1.04	1.07	0.99	1.03	1.29	1.07	1.05	1.36
53	1.21	0.85	0.73	0.68	1.29	0.75	0.70	0.78	0.59	0.74	0.56	0.77	1.34
52	0.25	0.37	0.53	0.48	1.25	0.44	0.44	0.45	0.25	0.38	0.32	0.36	0.38
51	0.55	0.47	0.54	0.47	0.35	0.30	0.31	0.30	0.18	0.49	0.37	0.53	0.71
50	0.31	0.22	0.19	0.09	0.56	0.14	0.09	0.13	0.08	0.27	0.19	0.31	0.32
49	0.01				0.22								
47													
46						0.01	0.01	0.01	0.39		0.03	0.03	
45		0.01	0.02	0.02	0.02	0.51	0.50	0.51	0.95	0.04	0.66	1.06	0.05
44	0.09	0.54	0.71	0.86	1.05	1.31	1.45	1.40	2.51	0.73	1.46	2.86	1.29
43	2.38	2.90	2.85	4.00	4.44	4.51	5.53	5.65	4.80	2.93	4.68	7.63	4.45
42	6.96	8.46	9.13	8.81	8.02	7.58	7.42	7.57	8.65	9.04	7.46	7.47	7.40
41	13.69	11.65	10.03	10.20	8.05	12.50	10.85	12.18	10.37	10.92	10.99	5.41	9.46
40	1.06	2.99	4.12	5.07	2.09	2.64	3.02	3.17	2.06	3.76	3.22	3.02	2.05
39	6.65	4.56	3.49	3.75	6.16	3.74	2.80	3.03	2.68	5.75	4.10	5.41	7.95
38	0.56	0.41	0.30	0.32	0.54	0.30	0.24	0.25	0.20	0.46	0.35	0.55	0.59
37	0.17	0.10	0.08	0.03	0.01	0.05	0.06	0.05	0.07	0.15	0.12	0.19	0.16
33													
32											0.03	0.03	
31		0.01	0.02	0.02	0.04	0.22	0.21	0.20	0.52	0.05	0.73	1.55	0.06
30	0.22	0.63	0.78	0.92	4.33	1.17	1.23	1.42	1.16	1.29	1.17	3.68	4.57
29	8.78	8.40	8.23	8.75	5.19	8.77	7.81	8.66	9.02	8.92	9.36	5.24	4.73
28	1.47	2.18	2.42	2.39	3.76	2.64	3.23	3.68	2.71	3.29	2.19	2.98	3.28
27	6.24	5.60	5.06	6.01	4.84	5.83	4.68	5.57	4.83	6.81	6.00	5.38	6.02
26	0.73	0.56	0.48	0.65	0.22	0.58	0.47	0.54	0.49	0.67	0.64	0.87	0.95
% C_7H_{14}		38.7	8.9	12.8	10.7	1.5	1.4	0.9	0.3	2.2	0.3	0.1	3.7
monolabelled		61.3	91.1	87.2	89.3	20.3	17.7	16.3	1.7	97.8	6.2	1.9	96.3
dilabelled						78.2	80.9	82.8	19.5		93.5	98.0	
trilabelled									78.5				

Table 2. *Distribution of* ^{13}C *in important fragment ions formed from labelled 1-heptenes*

% of total ionization	Ion formed	Position of ^{13}C							
(loss of)		1	2	3	7	1, 2	1, 3	2, 3	1, 2, 3
	C_6H_{11}	28	12	5	47				
0.8	$^{13}CC_5H_{11}$	72	88	95	53	34	40	13	
($CH_3\cdot$)	$^{13}C_2C_4H_{11}$					66	60	87	44
	$^{13}C_3C_3H_{11}$								56
	C_5H_{10}	59	60	20	4	51	2	2	
6.7	$^{13}CC_4H_{10}$	41	40	80	96	9	73	76	60
(C_2H_4)	$^{13}C_2C_3H_{10}$					40	26	22	19
	$^{13}C_3C_2H_{10}$								21
	C_5H_9	38	36	8	53	33	0	2	
5.1	$^{13}CC_4H_9$	62	64	92	47	8	38	42	32
($C_2H_5\cdot$)	$^{13}C_2C_3H_9$					59	62	56	10
	$^{13}C_3C_2H_9$								58
	C_4H_9	89	85	87	5	83	80	89	83
3.4	$^{13}CC_3H_9$	11	15	13	95	7	7	1	4
($C_3H_5\cdot$)	$^{13}C_2C_2H_9$					10	13	10	5
	$^{13}C_3CH_9$								8
	C_4H_8	65	64	66	30	62	61	64	61
14.7	$^{13}CC_3H_8$	35	36	34	70	4	6	4	3
(C_3H_6)	$^{13}C_2C_2H_8$					34	33	32	8
	$^{13}C_3CH_8$								28
	C_4H_7	56	60	43	51	52	26	28	30
9.4	$^{13}CC_3H_7$	44	40	57	49	13	36	34	30
($C_3H_7\cdot$)	$^{13}C_2C_2H_7$					35	38	38	13
	$^{13}C_3CH_7$								27
	C_3H_7	65	69	63	(44)	–	(70)	(61)	(56)
2.4	$^{13}CC_2H_7$	35	31	37	(56)	–	(5)	(11)	(12)
($C_4H_7\cdot$)	$^{13}C_2CH_7$					–	(25)	(28)	(8)
	$^{13}C_3H_7$								(24)
	C_3H_6	77	82	63	36	62	62	57	63
6.8	$^{13}CC_2H_6$	23	18	37	64	23	11	23	18
(C_4H_8)	$^{13}C_2CH_6$					15	26	20	3
	$^{13}C_3H_6$								16
	C_3H_5	71	72	69	54	67	54	54	52
14.1	$^{13}CC_2H_5$	29	28	31	46	14	25	22	16
($C_4H_9\cdot$)	$^{13}C_2CH_5$					19	21	24	14
	$^{13}C_3H_5$								18
	C_3H_3	49	45	40	82	41	30	26	26
6.8	$^{13}CC_2H_3$	51	55	60	18	17	29	21	16
($C_4H_9\cdot + H_2$?)	$^{13}C_2CH_3$					43	41	53	25
	$^{13}C_3H_3$								32
	C_2H_5	91	92	91	49	84	83	85	82
8.9	$^{13}CCH_5$	9	8	9	51	13	14	13	12
($C_3H_5\cdot + C_2H_4$?)	$^{13}C_2H_5$					3	3	2	6
	C_2H_3	79	80	85	61	75	69	65	61
6.4	$^{13}CCH_3$	21	20	15	39	15	26	31	22
($C_3H_5\cdot + C_2H_4 + H_2$?)	$^{13}C_2H_3$					10	5	4	16

Table 3. *Distribution of deuterium in important fragment ions formed from labelled 1-heptenes*

Ion formed	Position of D				
	1-d_1	1-d_2	5-d_2	7-d_1	7-d_3
C_6H_{11}	33	31	(5)	46	46
$C_6H_{10}D$	67	4	(27)	54	0
$C_6H_9D_2$		65	(67)		2
$C_6H_8D_3$					52
C_5H_{10}	57	59	–	7	
C_5H_9D	43	8	–	93	
$C_5H_8D_2$		32	–		
C_5H_9	39	39	–	52	
C_5H_8D	61	9	–	48	
$C_5H_7D_2$		52	–		
C_4H_9	82	(78)	(10)	7	
C_4H_8D	18	(11)	(19)	93	
$C_4H_7D_2$		(11)	(71)		
C_4H_8	66	63	(19)	30	
C_4H_7D	34	7	(65)	70	
$C_4H_6D_2$		30	(16)		
C_4H_7	68	57	(39)	53	
C_4H_6D	32	13	(36)	47	
$C_4H_5D_2$		30	(25)		
C_3H_7	66	67	(13)	(28)	
C_3H_6D	34	5	(42)	(72)	
$C_3H_5D_2$		28	(45)		
C_3H_6	79	76	22	26	
C_3H_5D	21	6	54	74	
$C_3H_4D_2$		18	24		
C_3H_5	72	70	48	58	
C_3H_4D	28	10	7	42	
$C_3H_3D_2$		21	45		
C_3H_3	59	54	65	81	
C_3H_2D	41	36	26	19	
C_3HD_2		10	9		
C_2H_5	90	84	33	46	
C_2H_4D	10	8	43	54	
$C_2H_3D_2$		8	25		
C_2H_3	84	78	61	76	
C_2H_2D	16	15	29	24	
C_2HD_2		7	6		

probabilities, or specific but preceeded by hydrogen rearrangement. However, the results for the compounds labelled in positions 1 and 7 as well as many of the results discussed below tend to indicate that the amount of H/D exchange occurring is relatively minor.

The finding that methyl loss can occur from either end of the molecular ion in 1-heptene is in agreement with previous studies of 3-[^{13}C]-propene [8], 1-butene-4-d_3 [9] and 1-pentene-5-d_1 [10]. However, somewhat more H/D exchange apparently takes place before methyl loss from the latter two compounds than in 1-heptene.

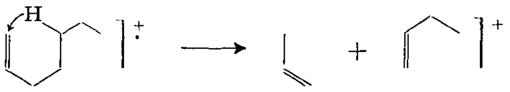
C_5 ions. – The C_2H_4 neutral fragments lost when $C_5H_{10}^+$ ions are formed contain at least one of the carbon atoms initially in positions 1, 2 or 3 with a probability of 79%. The first two positions appear to be nearly equivalent, but the probability of either C(1) or C(2) being lost along with C(3) is only about 2% for each case. Since the total probability of loss of C(3) is 20%, this atom is evidently most frequently lost in combination with one of the carbon atoms in positions 4–7. The fact that C(7) participates to the extent of only 4% leaves a total probability of 57% for loss of C(4), C(5) and/or C(6). H/D mixing prior to C_2H_4 loss seems to be a minor process.

These results are compatible with the conclusion of *Millard & Shaw* [6] that ethylene loss from 1-pentene occurs mostly from the unsaturated end of the molecule. Our results further suggest that some portion of what these authors interpreted as 1,2 hydrogen rearrangements (to account for loss of deuterium from positions 3, 4 and 5) may well have been due to skeletal rearrangements resulting in loss of C(3), C(4) and/or C(5).

Loss of C_2H_5 from the molecular ion strongly resembles loss of CH_3. About one third of the neutral fragments contain C(1) and C(2), while slightly more than one-half contain C(7) (and probably C(6)). Further, relatively little hydrogen shift away from either end of the molecule prior to fragmentation can be detected, so that the hydrogen transferred when C(1) and C(2) are lost as C_2H_5 does not come from position 7. Thus, the majority (> 80%) of the C_2H_5 loss observed appears to take place prior to skeletal rearrangement involving the terminal carbon atoms. On the other hand, a small but non negligible fraction (~10%) of the molecular ions which undergo this decomposition do show evidence that such rearrangements are occurring, but at a rate which is relatively slow compared to the rate of ethyl loss.

C_4 ions. – The $C_4H_9^+$ ions produced from the labelled compounds appear to be the result of simple allylic cleavage with charge retention on the saturated end of the molecule to the extent of at least 80%. Whatever rearrangement processes could preceed formation of this ion are therefore slow with respect to the fragmentation. The rather good agreement between the results for the molecules marked with ^{13}C and D in the same position (*i.e.* 1 or 7) shows that for the small fraction of ions which do evidence prior rearrangement, this rearrangement is likely to have been mainly skeletal, although some H/D exchange in position 1 is noted.

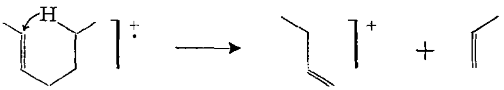
The figures in Tables 2 and 3 for the loss of C_3H_6 are remarkably similar for all of the labelled analogs marked in positions 1 through 3. Evidently, C(1), C(2) and C(3) are lost together with a probability of about 60%, or all three are retained in the ion with about 30% probability. The remaining 10% of the cases are mixed. The major reaction corresponds to the 6-center rearrangement mechanism (*reaction 1*) first proposed by *McLafferty* [11], with the charge remaining on the larger fragment.



(*1*)

The origin of the transferred hydrogen is seen to be mainly position 5 on the basis of the 5,5-d_2 figures.

Identification of the mechanism by which C(1), C(2) and C(3) are retained in the ion is more difficult. A 6-center rearrangement preceeded by a shift of the double bond to position two (*reaction 2*) is a possibility:



(*2*)

However, the $C_4H_8^+$ fragment ions formed *via reaction* (*2*) should contain no deuterium when the parent molecule is 1-heptene-5,5-d_2. In fact about only about 20% of these fragments contain no deuterium, so there is a discrepancy here. It is possible that the hydrogen transfer in both *reactions* (*1*) and (*2*) is less than 100% specific from positions 5 and 6 resp. This would explain the presence of $C_4H_6D_2^+$ (*reaction* (*1*) with hydrogen transfer from position 6) but would require that some of the $C_4H_7D^+$ come from *reaction* (*3*) *via* hydrogen transfer from position 5. A less promising but not impossible alternative would require the carbon atoms 1, 2, 3 and 5 to be present together in the daughter ion with a probability of up to 20%.

If the charge can remain on either fragment in *reactions* (*1*) and (*2*), one might expect the isotopic distributions in the $C_3H_6^+$ ions observed to be the complement of that for $C_4H_8^+$. In fact the observed distributions for the two ions are somewhat similar, for example, the majority of the $C_3H_6^+$ ions formed from products labelled in positions 1, 2 and/or 3 are unlabelled, while the opposite is true for those labelled in position 7. Thus the $C_3H_6^+$ data appear to be inconsistent with the possibility of formation *via reaction* (*1*) or (*2*). Nevertheless, several possible reaction pathways lead to this ion, and the interference could be large enough to obscure the expected distribution.

The results in Table 2 for $C_4H_7^+$ ions can be summarized as follows: 30% of these ions contain C(1), C(2) and C(3), 25% contain C(3) but not C(1) or C(2), and 50% contain C(7). Since the $C_4H_7^+$ ions are formed *via* several competing pathways (*cf.* Fig. 1), these data are difficult to interpret in a straightforward fashion. Nevertheless, several points are clear.

Whatever the pathways for formation of this ion may be, C(1) and C(2) behave in a very similar way, and differently from C(3). More interesting, perhaps, is the observation that for every fragment ion measured except $C_4H_7^+$ and $C_3H_3^+$, a very clear parallelism exists between the results for 1-[^{13}C]-1-heptene and the two analogs labelled with deuterium in position 1. Apparently, in most of the fragment ions C(1) and its original two hydrogen atoms remain together, whereas in the two exceptional ions, one of these hydrogen atoms has a significant probability of becoming separated from C(1) in some way. This behavior can be explained in terms of the following fragmentation sequence from Fig. 1:

$$\underset{(m/e\ 98)}{C_7H_{14}^{+\cdot}} \longrightarrow \underset{(97)}{C_7H_{13}^+} \longrightarrow \underset{(55)}{C_4H_7^+} \longrightarrow \underset{(39)}{C_3H_3^+} \qquad (3)$$

If the hydrogen atom lost in the first step of this sequence comes partially or wholly from position 1, the subsequent fragment ions formed from the 1-D-labelled compounds will be relatively deuterium-poor. This is what is observed: 44% of the $C_4H_7^+$ ions from 1-[^{13}C]-1-heptene retain the ^{13}C, while only 32% and 30% of those from the 1-d, and 1-d_2 labelled analogs, respectively, keep all of their tagged atoms. Furthermore, the amounts of unlabelled $C_4H_7^+$ from the 1-[^{13}C]-and the 1-d_2-labelled heptene are predicted to be the same on the basis of the mechanism suggested above; the measured values are 56 and 57%, respectively. Similar comparisons for the $C_3H_3^+$ data also are in excellent agreement with the predicted results although the multiplicity of possible routes of formation of this ion compel a certain amount of caution here.

C_3 ions. – The C_3 ions in general are not the products of any single fragmentation, but rather of a number of competing and consecutive reactions. Some suggestions as to the origins of the observed distributions in the ions $C_3H_3^+$ and $C_3H_6^+$ are included in the discussions of $C_4H_7^+$ and $C_4H_8^+$ ions, respectively. The $C_3H_5^+$ ion, which corresponds to the second-largest peak in the normal mass spectrum (*m/e* 41) might be guessed to be the result of allylic cleavage, as seems to be the case for its complement, $C_4H_9^+$. Allylic cleavage of 1,2,3-[^{13}C]-1-heptene would give $C_3H_5^+$ ions containing all three ^{13}C atoms, but in fact only 18% if these ions do contain all of the tagged atoms, although 48% contain at least one of the three. Thus, not only, is simple allylic cleavage not the major source of $C_3H_5^+$, but there is also a large amount of rearrangement of the carbon skeleton prior to formation of this ion. Surprisingly, little independent movement of the hydrogen atoms initially in positions 1, 7 and presumably 5 (since the two hydrogen atoms in this position remain together) is observed. The isotopic distribution in the $C_3H_5^+$ ions resembles that found for the $C_3H_6^+$ and $C_3H_7^+$ ions, at least to an extent which is not inconsistent with the expected facile loss of one or two hydrogen atoms from the latter ion. The most important difference between these three ions is the isotopic distribution in the ions from 1-heptene-5,5-d_2. The average number of deuterium atoms found per ion decreases from 1.32 in $C_3H_7^+$ to 1.02 and 0.97 in $C_3H_6^+$ and $C_3H_5^+$, resp. This is qualitatively reasonable since loss of hydrogen atoms occurs, but the specific distributions found are difficult to justify.

The origin of the $C_3H_7^+$ ion is also somewhat enigmatic. Up to ~ 50% could be formed by direct cleavage of the molecular ion to give an ion composed of C(5), C(6) and C(7) of the original molecule. In analogy with the results for loss of methyl and ethyl, another portion of up to ~ 25% could come from the unsaturated end of the molecule, following a hydrogen shift. In this case a significant amount of hydrogen transfer from position 5 would be implied by the 5,5-d_2 data.

C_2 ions. – The distribution of marked atoms observed in $C_2H_5^+$ is remarkably specific, considering the possible number of parallel reaction sequences which could lead to this species. The ion consists in large part (> 80%) of carbon and (presumably) hydrogen atoms originally located in positions 4–7. It appears likely, however, that these four positions are rather well mixed before $C_2H_5^+$ separation. The combination of specific loss of carbon atoms C(1)–C(3) and of the scrambling of carbon atoms C(4)–C(7) suggests the following two-step process:

$$C_7H_{14}^{+\cdot} \longrightarrow C_4H_9^+ \longrightarrow C_2H_5^+ \qquad (4)$$

Step one involves direct cleavage of the molecular ion to give $C_4H_9^+$ containing specifically carbon atoms C(4)–C(7). Step two is fission of $C_4H_9^+$ to give the ethyl ion, but only after extensive rearrangement of the C_4 ion. The scheme is supported by the fact that $C_4H_9^+$ does appear to be formed mainly by direct scission. In addition, statistical mixing of the four carbon atoms in $C_4H_9^+$ generated from various butyl halides has been previously reported [17]. The observed 51% retention of ^{13}C in $C_2H_5^+$ from 7-[^{13}C]-1-heptene is in excellent agreement with the value of 50% predicted by this hypothesis. The 7-d_1-labelled compound gives about the same amount of label retention as the former, suggesting that the methyl group may migrate intact, also in agreement with the finding [12] that H/D mixing was not complete in $C_4H_9^+$.

The isotopic distributions found for $C_2H_3^+$ ions from the various labelled 1-heptenes are sufficiently similar to those for $C_2H_5^+$ that it is reasonable to suppose that a significant portion of the former arise *via* loss of molecular hydrogen from the ethyl ions. The shift in the distributions observed for the D-labelled compounds between $C_2H_5^+$ and $C_2H_3^+$ accord with this assumption, and the multitude of possible decompositions giving rise to $C_2H_3^+$ easily explains the reduced overall specificity.

5. General remarks. – The results in Tables 2 and 3 demonstrate very clearly the importance of the role of rearrangement in the fragmentation scheme of the 1-heptene ion. The skeletal rearrangement in the molecular ion is certainly displayed in the results for loss of C_2H_4, but also to a lesser degree for loss of CH_3, C_2H_5, C_3H_5 and C_3H_6. The observed distributions of ^{13}C in the ions with two and three carbon atoms testify to possible further rearrangements either in the molecular ion, or more likely, in the direct precursors of these smaller ions in the case of consecutive fragmentation. ^{13}C-labelled alkyl ions show relatively little retention of positional identity [4] [12] [13] so that considerable rearrangement of the secondary ions $C_4H_9^+$ and $C_3H_7^+$ is likely. The rearrangement of the molecular ion might be envisioned to occur as successive isomerizations to and between various branched structures. The results of a study of competing metastable decompositions of C_7H_{14} isomers [14] as well as collision-induced dissociation measurements on several C_8H_{16} compounds [15], both tend to show that not all possible isomeric structures are easily interconvertible under mass spectrometric conditions. In particular, the very highly branched structures appear to be excluded as probable rearrangement products of the molecular ions.

It is remarkable that the difference of a single hydrogen atom between ionized 1-heptene and heptyl ion enhances skeletal rearrangement of the latter to such a degree that the distribution of ^{13}C in the fragment ions from $C_7H_{15}^+$ becomes close to statistical [13] [16]. Any adaptation of the idea of protonated or cationated cyclopropane intermediates which has been proposed to account for alkyl ion rearrangements [4] must take account of this difference. However, it is not unreasonable to suppose that the removal of a hydrogen atom from the 3-membered ring structure might retard the formation and/or subsequent re-opening of the ring sufficiently to cause the observed slower rate of rearrangement in alkene ions.

The final point to be discussed concerns the question of intramolecular hydrogen shift or 'hydrogen scrambling'. A comparison of the results for compounds labelled independently with ^{13}C and D in positions 1 and 7 shows that the percentages of label retention are strikingly similar for most of the ions studied. The only exceptions are $C_4H_7^+$ and $C_3H_3^+$ for position 1, and $C_3H_7^+$, $C_3H_6^+$ and $C_2H_3^+$ for position 7. The first two of these are discussed above, while the latter three are probably mainly secondary ions whose origins are unclear in any case. Apart from these exceptions, however, only very limited shift of hydrogen atoms away from positions 1 and 7 can occur before fragmentation. This conclusion does not exclude migration to position 1, except from position 7, and in fact it is possible that the reason for the apparent lack of shift of the hydrogen atoms on position 1 is that a rapid transfer of hydrogen atoms to this position occurs and that the newly formed methyl group is less susceptible to subsequent hydrogen abstraction than the methylene groups. The observation that both methyl and ethyl loss can occur from both ends of 1-heptene lends support to the notion of rapid transfer to position 1. Previous experiments performed with deuterium labelled hexane [16] and heptyl [13] ions appear to confirm that the probability of hydrogen migration from methyl is reduced as compared to the probability of migration from a methylene group.

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