FRAGMENTATION OF 5α-CHOLESTANE IN MASS SPECTRA

BY ELECTRON IMPACT OF EXTREMELY LOW ENERGY[*]

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Effect of ionizing voltage V_i on mass spectra of organic compounds offers a usefull knowledge to their fragmentation scheme, as demonstrated successfully by Natalis[1] in the study of trans and cis decalines. This effect would become especially evident if V_i is extremely low, and the change of spectra may give us some key to interpret the scheme. We reported already[2] on cyclododecane and n-hexadecane that when V_i was lowered, distribution of their fragment ions vs. C_i group gave the one as theoretically predicted by our theory. As another example of such effect, a study on cholestane will be reported.

According to a Swedish spectrum of 5α-cholestane,[3] its base peak is m/e 217 (100), followed by peak m/e 218 (54).[**] These two peaks are explained by rupture of the D ring (dotted line a̰), accompanying loss of a hydrogen in the case of m/e 217. The next high peak is m/e 149 (38), being accompanied by a small satellite peak m/e 150 (15). They are explainable by rupture of the C ring (dotted line b̰). Parent peak m/e 372 (35) and peak m/e 357 (36), ascribable to M-15 ion, appear also in nearly equal intensity to peak m/e 149. The spectrum in the API table (No. 1000) is qualitatively similar to the above.

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[*]   Report XVII on molecular-orbital theory for mass spectra.

[**] Figures in parentheses are intensity of the peak.

We measured the spectra of 5α-cholestane by lowering not only the ionizing voltage V_i but also adjusting the repeller potential V_r to be zero. The apparatus was a double focussing spectrometer equipped with a direct sample-inlet (JES-OISG), and a sample of the analytical grade was used without any treatment.

	m/e
a	218, 217
b	150, 149
c	232, 233
d, d'	357
e	262
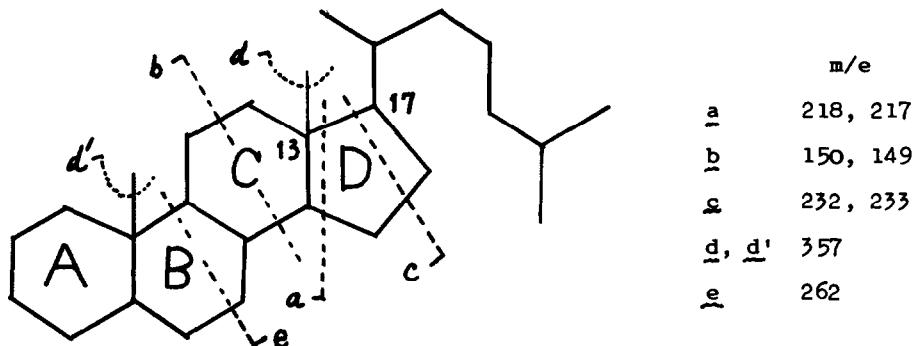
General features of the spectra at V_i = 50 volts were nearly the same as those of API and Swedish ones, except that our parent peak was ca. three times more intense than theirs. However, when V_i is decreased below 16 volts, different features appeared drastically in our spectra. Details of the spectra are shown in TABLE I, where height of the parent peak is taken to be 100 instead of that of the highest peak, as usually adopted. All the fragment ions disappeared below 13 volts and then the parent ion at 10 volts. Of course, sensitivity of the parent peak decreases markedly in accordance with V_i.

Important effects of lowering V_i on the spectra are summarized as follows:

1°) Of all fragment peaks, fraction of the peaks relating to rupture a (m/e 217, 218 and 219) increases relatively to the other peaks.

2°) Peak m/e 218 becomes higher than peak m/e 217 at 16 volts just in contrast with the ordinary spectra, and remains at 13 volts.

3°) Peak m/e 232, which is ascribable to rupture c, remains even at 14 volts, though relatively low at 50 volts.

4°) Peak m/e 357 remains as a high peak already at V_e = 20 volts and appears at 14 volts with peaks m/e 232, 217 and 218.

5°) Peaks m/e 149 and 150 decrease markedly. Besides, a reversal of height in their peaks is expected below 15 volts, as in the case 2°).

TABLE I   Effect of Ionizing Voltage V_i on the Main Peaks[*]

in the Spectra of 5α-Cholestane

Measuring Condition: $V_r = 0$; temp. of ionizing chamber = 150 ~ 240°C;

scanning time from m/e 15 to m/e 400 = 3 min.

m/e \ V_i	50	20	16	15	14	13
373	30	30	30	35	33.5	31
372	100	**	**	100	100	100
357	32.5	27	19	11	4	
262	11	10	7	4		
259	2	2	1	1		
232	19	16	12.5	8	5	
219	18	15	5	2	3	
218	35	**	47	38	26	15
217	104	**	43.5	25	9	
204	3	2	1	1		
203	13	2.5	3.5	1		
190	3.5	2	1	1		
163	8	3	1			
162	7	3	1	0.5		
151	8	4	2	1		
150	13	8	3	2		
149	43	20	6.5	2		
148	11	5.5	2	1		
137	8	3.5	1	1		

m/e \ V_i	50	20	16
136	6	2.5	1
135	14	4	1
123	17	6	1
122	13	5	2
121	16	3.5	0.5
109	36	6	1
108	15	4	1
107	14	1	
97	9	2	
95	36	4	0.5
93	15		
83	15	2	
81	30	2	
79	9.5		
69	17.5	1	
67	20		
57	15		
55	23		
43	18		

*   Contribution of ^{13}C to the peak height is corrected except the isotopic parent peak (m/e 373), whose ratio to m/e 372 may become a measure of reliability of the spectra.

**   The height of these peaks could not be determined due to scaling out. The figures of V_i = 20 and 16 volts were determined, therefore, by assuming the height of m/e 373 to be 30.

6°) Of the relatively high peaks, peak m/e 262 ascribable to rupture e still appears at 15 volts, while peaks m/e 109, 95 and 81 which are even higher than peak m/e 372 and 357 in the ordinary spectra decrease rapidly.

Since fragmentation at lower V_i corresponds to the situation that the fragment ions thus produced are given smaller energy, they are produced primarily from the parent ion. Therefore, we can conclude from 1°) and 3°) that the D ring ruptures the most easily at the 13-17 bond, as a common consequence of both ruptures a and c. From the same reasoning on 4°), stripping of some methyl group, which may be the scission d' or d as generally accepted, occurs as the second easiest fragmentation.

On the contrary, peaks m/e 109, 95 and 81 mentioned in 6°) would be due to the secondary ions produced from the primary fragment ions, which have much excess energy. Judging from 2°) and 5°), peaks m/e 217 and 149, which show an intermediate behavior concerning the relation between peak height vs. V_i, seems to be produced from peaks m/e 218 and 150, respectively.

However, it is still difficult to conclude the detailed fragmentation scheme from the above drastic change of the spectra with V_i alone. We expect with much interest how the above new findings can be interepreted consistently and at least qualitatively with the deuterium labelling and other techniques, as done by Djerassi[4] to explain the formation of peaks m/e 217, 218 and 357.

We are now investigating this problem from the standpoint of our molecular orbital theory[2] and the result will be published elsewhere, comparing the fragmentation scheme proposed hitherto.

REFERENCES

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4) C. Djerassi, Adv. in Mass Spectrometry, Vol. 4, p. 199, The Institute of Petroleum, London (1968).