The Formation of C_5^+ by Electron Impact on Perchloro-cyclopentadiene and -benzene,

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PERCHLOROCYCLOPENTADIENE, C_5Cl_6, is known to react as a chlorinating agent.[1] The reactivity of the chlorine atoms at the quaternary carbon atom allows the formation of adducts with Lewis acids,[2,3] some of which decompose with a triplet e.p.r. signal[3] which suggests the perchlorocyclopentadienyl cation, $C_5Cl_5^+$, as a decomposition intermediate.

The high tendency of C_5Cl_6 to form $C_5Cl_5^+$ is also shown by the mass spectrum (Table). The ion

Mass spectrum of hexachlorocyclopentadiene, C_5Cl_6

m/e	Species*	Relative intensity	*m/e*	Species*	Relative intensity	*m/e*	Species*	Relative intensity
47		11·4	106		7·3	200		0·9
47·5	CCl^+	0·6	108	$C_3Cl_2^+$	4·4	201		3·1
48		2·5	110		1·1	202	$C_5Cl_4^+$	0·9
49		3·9				203		3·9
			117		12·0	204		0·7
59	C_2Cl^+	1·6	117·5		8·4	205		1·7
60	C_5^+	22·1	118		5·3	206		0·6
61		2·1	118·5		13·7			
			119	CCl_3^+	10·8	235		62·5
65		12·2	119·5	$C_5Cl_5^{2+}$	10·4	236		4·6
65·5		0·6	120		3·5	237		100·0
66	$C_5Cl_2^{2+}$	7·1	120·5		3·0	238	$C_5Cl_5^+$	6·8
66·5		0·6	121		3·5	239		65·1
67		1·3				240		4·6
			130		24·3	241		20·6
71	C_3Cl^+	9·3	131		2·2	242		1·6
73		3·9	132	$C_5Cl_2^+$	16·1	243		3·9
			133		1·3	244		0·4
82		1·0	134		3·0			
82·5	CCl_2^+,C_4Cl^-	2·4	135		1·0			
83		5·6				270		9·3
83·5	$C_5Cl_3^{2+}$	2·1	141		15·7	271		0·6
84		1·3	142		0·9	272		17·9
84·5		1·3	143	$C_3Cl_3^+$	15·7	273	$C_5Cl_6^+$	1·4
85		2·2	144		0·9	274		14·4
			145		4·9	275		1·1
94		3·1	147		0·9	276		6·7
95	$C_2Cl_2^+$,C_5Cl^+	32·5				277		0·5
96		3·5	165		14·6	278		2·0
97		9·5	166		1·5			
98		1·5	167	$C_5Cl_3^+$	13·3			
			168		1·1			
100		5·1	169		5·0			
100·5		0·9	170		0·4			
101	$C_5Cl_4^{2+}$	6·8	171		1·0			
101·5		0·8						
102		3·6						
102·5		0·8						
103		0·9						

* The listed formulae refer to a group of *m/e* values. Only the most important formulae are given.

of largest abundance in the 20—80 v ionization range was $C_5Cl_5^+$. Further release of chlorine was observed in an interesting ion sequence: $C_5Cl_5^+$, $C_5Cl_4^+$, $C_5Cl_3^+$, $C_5Cl_2^+$, C_5Cl^+, and C_5^+.

This is the principal difference between the mass spectra of hexachloro- and hexamethyl-cyclopentadiene.[4] In the mass spectrum of the latter compound, masses lower than that of the five-membered cation do not retain their cyclopentadienyl structure but undergo rearrangement, probably to a cyclic benzenium-type ion.[4]

The existence of C_5^+ is deduced from a distinct peak at *m/e* 60 with a side peak at *m/e* 61. This signal cannot be assigned to a compound containing chlorine, since there is no peak at *m/e* 62. With multiply-increased sensitivity an *m/e* 62 signal can be observed, its intensity varying between 1·0 and 2·0% of that at *m/e* 60. This value, of course, is very uncertain. It should be 0·15% o; the 60 *m/e* signal due to carbon isotopes from C_5^+f and 30%, for a compound containing chlorine.

In different spectra, the *m/e* 61 intensity is between 5·5 and 9% of the 60 *m/e* signal. This value should be 5·5% for a C_5^+ *m/e* 60. An interference of the *m/e* 59 ion must be considered in this peak, if *m/e* 59 is assigned to C_2Cl^+.

In some parts of the spectrum doubly charged ions are observed, for example, $C_5Cl_5^{2+}$, $C_5Cl_4^{2+}$, $C_5Cl_3^{2+}$, $C_5Cl_2^{2+}$. The 59, 60, 61 *m/e* sequence cannot be assigned to a doubly charged $C_4Cl_2^{2+}$, since no half masses are seen, due to ^{13}C.

For hexafluorobenzene, $C_6F_6^+$, an ion sequence $C_5F_5^+$, $C_5F_4^+$, $C_5F_3^+$, $C_5F_2^+$, and C_5F^+, is observed.[5] In the spectrum of hexachlorobenzene $C_5Cl_5^+$, $C_5Cl_4^+$, $C_5Cl_3^+$, C_5Cl^+, and C_5^+ are observed, with weak relative intensities.

It is impossible at present to give structural details concerning the observed C_5^+ system. Thus, it is impossible to decide whether this compound is cyclic or linear.

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