Chlorine Randomization Between Phenyl Groups in the Electron Impact-induced Fragmentation of Polychlorinated Biphenyls

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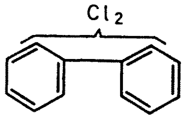
Summary The mass spectra of dichlorobiphenyls show chlorine randomization over both phenyl rings with the exception of 2,2′- and 2,6-biphenyl (I, e and f) in which both chlorine atoms are *ortho* to the Ph–Ph bond; similar results are obtained with tetrachlorobiphenyls which show chlorine randomization in the $M - Cl_2$ ion.

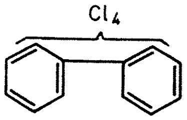
THE mass spectra of several monocyclic aromatic compounds (*e.g.* benzene,[1] pyridine,[2] benzonitrile,[3] and halogenobenzenes[4]) exhibit considerable H–D randomization in the molecular ion prior to fragmentation. Bicyclic aromatic compounds such as diphenylacetylenes,[5] benzothiophen,[6] and biphenyl[6] also show proton equilibration upon electron impact (deuteriated biphenyl shows 70—75% H–D randomization in the molecular ion) and substituted biphenyls[7] give similar results which vary slightly depending on the substituent present. It was demonstrated that isomeric halogenobiphenyls lose positional identity upon electron impact[7] and these results could be explained by carbon scrambling in the molecular ion *via* photochemical processes.[6]

It was therefore of interest to examine the mass spectra of polyhalogenated biphenyls which might distinguish between the photochemical analogy and other alternatives such as the formation of acyclic ions by both C–C and C–Cl bond fission.



(I)

(a) 4, 4'
(b) 3, 3'
(c) 3, 4
(d) 2, 4
(e) 2, 2'
(f) 2, 6



(II)

(a) 3, 5, 3', 5'
(b) 2, 3, 4, 5
(c) 2, 3, 5, 6
(d) 2, 4, 2', 4'
(e) 3, 4, 3', 4'

The mass spectra of a series of polychlorinated biphenyls (PCBs) were investigated to determine the extent of chlorine randomization. Since PCB mixtures are ubiquitous environmental pollutants their breakdown pattern and spectral characteristics are of considerable interest. The primary ion spectra of the 6 isomeric dichlorobiphenyls (I, a—f) are shown (Table 1). The fragmentation pathway (Scheme 1) shows loss of both Cl· and HCl from the molecular ion and expulsion of Cl· from the *M* — Cl ion with intense metastable peaks at *m/e* 157·7 (m_1*) and *m/e* 122·7 (m_5*) for the reactions (**a**) → (**b**) and (**b**) → (**c**) respectively. This breakdown pattern is common for all isomers. Using the kinetic approach[8] the m_1* : (**b**) and m_2* : (**c**) ratios for the above reactions were determined at 70 and 20 eV (Table 1). The results indicate that for the isomers (I, a—d) their decomposing molecular ions (**a**) and *M* — Cl ions (**c**) have similar energy distributions and structures. This clearly suggests chlorine randomization over both benzene rings to give symmetrical ionic intermediates in which each carbon atom is equally substituted with chlorine. Isomers (I, e and f) were exceptions to the above since the primary ion spectra give relatively more intense *M* — Cl ions and the metastable : daughter ion ratios are different from those of the other isomers (I; a—d). It appears that the fragmentation pattern is affected by the presence of two chlorine atoms *ortho* to the Ph–Ph bond but not the presence of just one (Ic). Similarly with the monohalogenobiphenyls the *ortho*-isomer is indistinguishable from the *meta*- and *para*-compounds.[7]

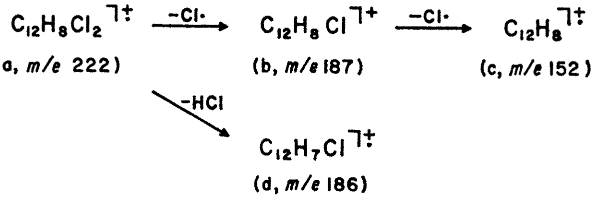


TABLE 1. *Relative ion intensities*[a] *and metastable ion* : *daughter ion ratios for the dichlorobiphenyls* (*I*, *a—j*)

Compound	*M*	*M* — Cl	*M* — HCl	*M* — Cl_2	$\frac{[m^*]_1}{[m/e\ 187]} \times 10^3$ 70 eV	20 eV	$\frac{[m^*]_2}{[m/e\ 152]} \times 10^5$ 70 eV	20 eV
(IIIa)	100	1·4	6·0	38	15·5	13·5	2·1	1·7
(IIIb)	100	1·4	6·1	38	15·5	12·0	2·2	1·5
(IIIc)	100	1·5	6·7	35	16·0	13·0	2·3	1·5
(IIId)	100	1·5	7·2	39	17·0	14·0	2·3	1·7
(IIIe)	100	2·8	7·5	79	5·1	4·0	180	110
(IIIf)	100	2·4	6·3	35	100	27·0	100	100

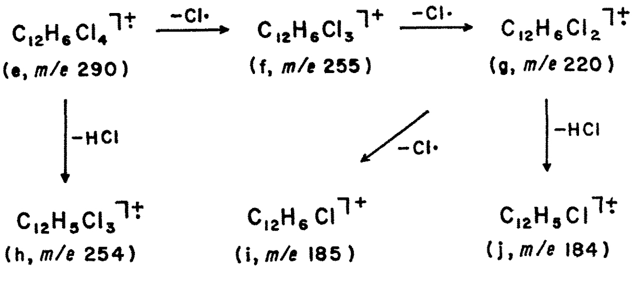
[a] Recorded at 70 eV.

TABLE 2. *Relative ion intensity*[a] *and metastable : daughter ion ratios for tetrachlorobiphenyls*

Compound	*M*	*M* — Cl	*M* — HCl	*M* — Cl_2	*M* — Cl_3	*M* — (Cl_2 + HCl)	$\frac{[m_3^*]}{[155\cdot5} \times 10^3$ 70 eV	20 eV
(IIa)	79	0·8	4·9	28	3·6	7·3	6·7	6·6
(IIb)	79	0·9	3·4	32	3·2	6·3	6·7	6·9
(IIc)	78	1·2	2·3	37	3·9	8·0	6·8	6·8
(IId)	79	3·4	1·9	47	4·8	7·9	6·6	6·6
(IIe)	79	0·3	1·0	25	4·2	6·2	6·6	6·6

[a] Recorded at 70 eV.

Tetrachlorobiphenyls (II; a—e) also fragment with successive loss of chlorine atoms and their primary ion spectra are virtually indistinguishable (Table 2). The metastable peaks for the transitions (**e**) → (**f**) and (**f**) → (**g**) are broad and the metastable : daughter ion ratios were difficult to measure owing to the multiplicity of chlorine isotopes. The spectra of all isomers (II, a—e) have a sharp metastable ion at *m/e* 155·5 (m_3*) which corresponds to the reaction (**g**) → (**i**). The ratio m_3* : (**i**) for all the



tetrachloro-isomers is in the range 6·6—6·8 × 10^{-3} (Table 2) indicating that the structures of the decomposing $C_{12}H_6Cl_2$ ions (**g**) formed by the tetrachlorobiphenyls (II, a—e) upon electron impact are similar with scrambling of the chloro-groups over all carbon atoms of the molecule. These data are comparable to the results with the dichloro-isomers (I, a—d) except that the effects of the orientation of the chlorine atoms *ortho* to the Ph–Ph bond (I, b—d) have been eliminated prior to the (**g**) → (**i**) decomposition. Analogous results have been observed in the mass spectra of tri-, penta-, hexa-, and octa-chlorobiphenyls.[9]

This approach shows that in most isomers the chloro-groups are scrambled over both aromatic rings implying that symmetrical intermediates are formed by processes other than, or in addition to, photochemical-type equilibration. The exceptional isomers (I, e and f) contain two chloro-substituents *ortho* to the Ph–Ph bond. These results also show that in most cases the primary ion spectra of di- and tetra-chlorinated biphenyls do not distinguish between isomers which are inseparable by g.l.c., an important consideration in PCB analysis.

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