Polyhalogenoaromatic Compounds. Part XXXVI.[1] Mass Spectra of Octa- and Hepta-chloronaphthalenes

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Mass spectra of octa- and the two hepta-chloronaphthalenes and hexachlorobenzene are recorded and discussed. Serial losses of chlorine atoms provide the major fragmentation sequence in each case and spectra of all three naphthalene compounds contain peaks due to C_{10}^{+} and C_{10}^{2+} ions. G.l.c.–mass spectrometry was used to separate the components of a commercial product containing polychloronaphthalenes and record their spectra. Some limitations of the use of mass spectrometry for the analysis of polychloro-compounds are discussed.

POLYHALOGENOAROMATIC compounds are widely used as pesticides, electrical insulation materials, plasticisers, *etc.*[2] Concern has been expressed about the dangers caused by residues of chlorine-containing compounds which resist biological and chemical degradation and so accumulate and persist in our environment.[3] Mass spectrometry is very useful for the study of polychloro-compounds since their spectra often show successive losses of chlorine atoms. The resulting groups of peaks, with readily recognisable isotope patterns, provide a ready means for the detection of environmentally important compounds.[4] However mass spectra of even some very widely used polychloroaromatic compounds have not been reported in detail. For example only a brief report has been given on the mass spectrum of octachloronaphthalene,[4] the major constituent of products marketed under such names as Halowax 1051.[5]

The spectrum of octachloronaphthalene [Figure (a)], which has now been examined in more detail, shows several very interesting features. The molecular ion is the base peak and the only important mode of fragmentation is by successive losses of chlorine atoms. Metastable peaks show that the chlorine atoms are to a large extent lost singly but there are also a few small metastable peaks which may indicate that simultaneous loss of two chlorine atoms sometimes occurs. For example a group of very low intensity peaks in the *m/e* 272 region correspond with the transition $C_{10}Cl_8$ to $C_{10}Cl_6$. Remarkably, all eight chlorine atoms may be lost successively without loss of a carbon atom. This is clearly shown by groups of peaks with appropriate *m/e* ratios and isotope patterns for $C_{10}Cl_8^{+}$—$C_{10}Cl^{+}$ ions and a single peak at *m/e* 120 whose accurate mass showed it to be due to the C_{10}^{+} ion. The structure of the C_{10}^{+} ion must be a matter for conjecture but it may be noted that polycarbon ions, both singly and doubly charged, up to C_{28}^{+}, have been observed in an arc struck between graphite electrodes.[6] The presence of C_5^{+} ions has also been noted in the spectra of hexachlorocyclopentadiene and hexachlorobenzene.[7]

Besides the series of singly charged ions octachloronaphthalene gave a corresponding series of doubly charged ions. The compositions of these are readily recognised because they have the characteristic chlorine isotope patterns but the members of each group of peaks are separated by only one mass unit instead of two. A peak at *m/e* 60 is due to C_{10}^{2+} ions because it has a ^{13}C isotope peak at *m/e* 60.5.

The relative intensities of the ions along the series $C_{10}Cl_8^{+}$, $C_{10}Cl_7^{+}$, *etc.*, are interesting. It is usually considered that even electron ions tend to be more stable than odd electron ions [8] but in this case, although there is a general fall in the relative intensities along the series of fragment ions, the odd electron ions are always more intense than neighbouring even electron ions. Similarly, in the case of heptachloronaphthalene [Figure (b)] the odd electron ions are again more intense than neighbouring even electron ones. Furthermore doubly charged versions of $C_{10}Cl_8$, $C_{10}Cl_6$, *etc.*, which are even electron species, are much less intense than corresponding singly charged odd electron molecules but the odd electron, doubly charged versions of $C_{10}Cl_5$, $C_{10}Cl_3$, *etc.*, have about the same intensities as their singly charged, even electron, counterparts. No similar anomalies appear in the spectrum of the monocyclic compound, hexachlorobenzene [Figure (d)].

Another noteworthy feature observed in the spectrum of octachloronaphthalene was the presence of a group of low intensity peaks due to $C_{10}HCl_7^{+\cdot}$ ions. These could have been due to ion–molecule interactions in which $C_{10}Cl_8^{+\cdot}$ or $C_{10}Cl_7^{+}$ ions abstract hydrogen atoms from adventitious compounds in the source or alternatively radical reactions in which $C_{10}Cl_7\cdot$ radicals, produced by thermolysis of octachloronaphthalene, similarly abstract hydrogen atoms to give heptachloronaphthalene, which is subsequently ionised. The following evidence suggests that slow incorporation of hydrogen atoms by thermal reactions on the surfaces of the inlet systems and source of the mass spectrometer is mainly responsible.

(a) If a little octachloronaphthalene was kept in the all-glass heated inlet system of the spectrometer at 220° and slowly introduced into the source, the abundance of $C_{10}HCl_7^{+}$ ions relative to $C_{10}Cl_8^{+}$ ions steadily increased with time until the two were of comparable intensity.

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[1] Part XXXV, B. J. Wakefield, *J. Organometallic Chem.*, 1975, **99**, 191.

[2] M. B. Green, in ' Polychloroaromatic Compounds,' ed. H. Suschitzky, Plenum, London, 1975, ch. 4.

[3] ' Chemical Fallout,' eds. M. W. Miller and G. G. Berg, Thomas, Springfield, 1969; C. A. Edwards, ' Persistent Pesticides in the Environment,' Blackwell, Oxford, 1974, 2nd edn.

[4] O. Hutzinger, S. Safe, and V. Zitko, *Internat. J. Environmental Analyt. Chem.*, 1972, **5**, 95.

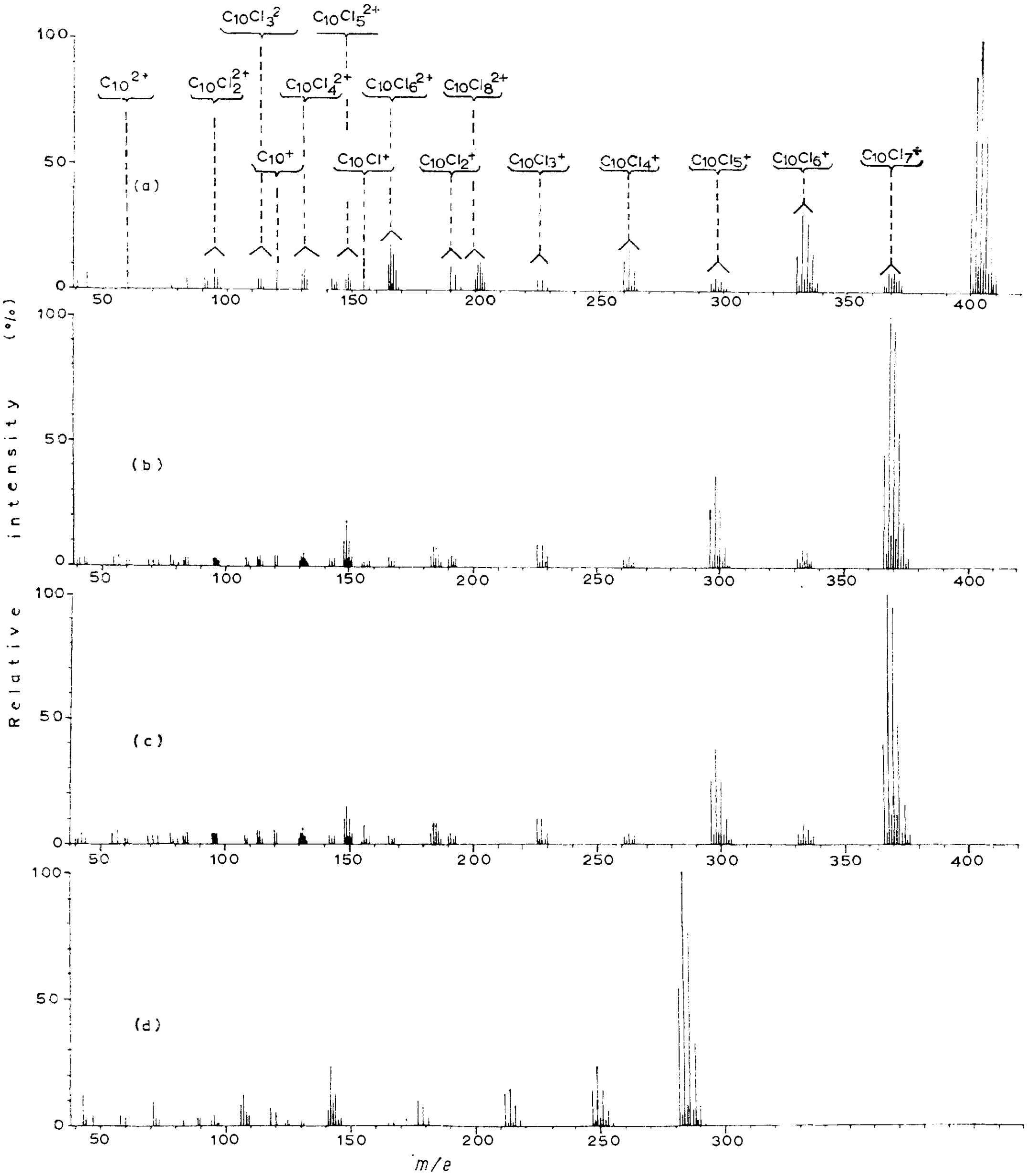
[5] ' Halowax Chlorinated Naphthalene Oils and Waxlike Solids,' Koppers Co., Pittsburgh.

[6] E. Dornenburg and H. Hintenberger, *Z. Naturforsch.*, 1959, **14a**, 765.

[7] L. Schafer, *Chem. Comm.*, 1968, 1622.

[8] F. W. McLafferty, ' Mass Spectrometry of Organic Ions,' Academic Press, New York, 1963, p. 318.

(b) If octachloronaphthalene and deuterium oxide were simultaneously introduced from separate inlet systems, into a mass spectrometer source, kept at 100°, there was no detectable incorporation of deuterium so an ion–molecule interaction in the gas phase is unlikely.



Mass spectra of polychloroaromatic compounds: (a) octachloronaphthalene; (b) heptachloronaphthalene made by reduction of octachloronaphthalene (probably 1*H*-isomer); (c) heptachloronaphthalene separated from Halowax 1051 (probably 2*H*-isomer); (d) hexachlorobenzene. *m/e* Ratios and relative intensities are tabulated in Supplementary Publication No. SUP 21592 (5 pp.; for details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue).

(c) If octachloronaphthalene and deuterium oxide were kept together in a heated inlet system maintained at 240° there was gradual formation of $C_{10}Cl_7D$ (and $C_{10}HCl_7$) although more complex reactions also occurred as the reaction time was extended.

If the source pressure of octachloronaphthalene was increased the relative abundance of $C_{10}HCl_7^+$ ions was considerably reduced but this was only because the effects of surface reactions were swamped. These results resemble those obtained with quinones which frequently undergo reduction by water in the inlet systems of mass spectrometers[9] but usually give the expected spectra when introduced on a direct insertion probe. The above results indicate that spectra of labile polychloroaromatic compounds must be interpreted with caution especially if the compounds are present in low concentration and are introduced other than on a direct insertion probe. Another limitation of the use of mass

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[9] R. T. Aplin and W. T. Pike, *Chem. and Ind.*, 1966, 2009.

spectrometry for the analysis of polychloro compounds is the fact that they are often very difficult to remove from the spectrometer source and affect subsequent spectra for many hours as we have observed with the extensive range of aromatic and heteroaromatic compounds described in this series.[1,10]

It was shown by g.l.c.–mass spectrometry that five times recrystallised octachlorophthalene still contained a trace of genuine heptachloronaphthalene. However, the spectrum of the pure octachloro-compound from the g.l.c. still showed small $C_{10}HCl_7^+$ peaks due to the reactions discussed above.

From a chromatogram obtained when Halowax 1051, a product which contains several polychloronaphthalenes, was subjected to g.l.c.–mass spectrometry, it is clear that naphthalenes with differing numbers of chlorine atoms are very easily separated on the SE30 column. A mixture of the two isomeric heptachloronaphthalenes, however, was not separated by this system. One of the isomers, probably the 1*H*-compound, was obtained by reduction of octachloronaphthalene [11] and the other was separated from Halowax 1051 [12] but a mixture of the two gave only one peak on g.l.c.

Mass spectra of the two heptachloronaphthalenes were indistinguishable except for minor differences in relative intensities of some of the peaks [Figure (b) and (c)]. Again the major mode of fragmentation is by successive losses of chlorine atoms and all seven may be lost to give a $C_{10}H^+$ ion. Chlorine atom loss seems to be strongly preferred to loss of the hydrogen atom for loss of the latter does not intrude appreciably until at least four chlorine atoms have been shed. Loss of all chlorine atoms and the hydrogen gives the C_{10}^+ ion. Once more the odd electron ions are most abundant and doubly charged versions of all the ions are apparent.

The spectrum of hexachlorobenzene [Figure (d)] which has been published in part, [7,13] is shown for comparison purposes. Serial losses of chlorine atoms are again dominant with peaks for C_6Cl_6—C_6Cl ions clearly visible. The C_6^+ ion, however, makes only a small contribution to the *m/e* 72 peak which consists mainly of $(C_6{}^{35}Cl{}^{37}Cl)^{2+}$ and $({}^{12}C_2{}^{13}C{}^{35}Cl)^+$ ions. Breakdown of the carbon skeleton is more obvious than in the polychloronaphthalenes particularly after four chlorine atoms have been lost. Thus C_5Cl_2, C_4Cl_2, and C_2Cl_2 ions are all present. Moreover carbon skeleton fragmentation *can* occur very early as evidenced by the presence of $C_5Cl_5^+$ ions in *ca.* 1% relative abundance. Many other ions with varying numbers of chlorine and carbon atoms are also present in low abundance.

EXPERIMENTAL

Octachloronaphthalene, m.p. 197.5—198° (lit., 196—197°;[14] 197.5—198° [15]), was obtained by fractional crystallisation of Halowax 1051 from carbon tetrachloride. Hexachlorobenzene, m.p. 226° (lit.,[16] 227°), was a recrystallised commercial sample.

Mass spectra were measured on an AEI MS 902S spectrometer with accelerating voltage 8 kV, ionising voltage 70 eV, and trap current 100 or 500 μA. Source temperature was *ca.* 220° unless specified otherwise. Samples were introduced on a direct insertion probe except where otherwise specified in the text. For g.l.c.–mass spectrometry the instrument was coupled to a Pye 104 gas liquid chromatograph *via* a silicone membrane separator. Chromatograms were recorded from the total ion current monitor of the spectrometer. Octachloronaphthalene, Halowax 1051, and heptachloronaphthalenes were chromatographed on an 18 ft × 1/8 in glass column packed with 3% SE30 on Chromosorb W, at 230°, with 25 ml min^{-1} of helium as carrier gas. The molecular separator was kept at 250°.

We thank Koppers Co., Inc., for gifts of Halowax 1051.

[5/1221 *Received*, 23*rd June*, 1975]

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[10] J. Clark, unpublished observations.

[11] N. A. Tahir, M.Sc. Thesis, Salford, 1975.

[12] B. J. Wakefield, unpublished work.

[13] S. Meyerson and E. K. Fields, *J. Chem. Soc.* (*B*), 1966, 1001.

[14] W. L. Mosby, *J. Amer. Chem. Soc.*, 1955, **77**, 759.

[15] V. Shvenberger and V. Gordon, *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 529.

[16] M. Ballester and S. Olivella in ' Polychloroaromatic Compounds,' ed. H. Suschitzky, Plenum, London, 1975, ch. 4.