The GC and Direct Inlets Mass Spectra of Heptachlor and 1-Hydroxychlordene

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Some interesting and important differences between the direct inlet and GC inlet mass spectra of heptachlor and 1-hydroxychlordene were observed. These differences are reported.

Experimental

All spectra were obtained with a Hitachi Perkin-Elmer RMU-6L Mass Spectrometer. The direct inlet spectra were obtained at an accelerating voltage of 3100 V (range 750), an electron energy of 70 V, and a sample temperature below 80°C. For the spectra obtained through the "batch inlet system" the temperature of the sub-oven was of 120°C.

The GC inlet spectra were obtained by injecting in the gas chromatograph two microliters of a 1 μg/μl solution in heptane of each of the compounds studied. The gas chromatograph, Perkin-Elmer Model 990, was connected to the mass spectrometer through a Watson-Bieman, one stage separator (standard separator supplied with the system used here).

The gas chromatographic conditions were as follows: injector temperature 220°C, column temperature 200°C, manifold and separator temperature 230°C, connecting tube (between separator and mass spectrometer) 250°C. A six feet, 4 mm i.d., glass column packed with 3% OV-17 on Chromosorb W, HP 80/100 was used. The mass spectrometric conditions were: accelerating voltage 4800 V (range 500), electron energy 70 V, chamber temperature 230°C.

The compounds, heptachlor (Polyscience) and 1-hydroxychlordene (Velsicol Chemical Corp.), were used without any further purification.

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Results and Discussion

The direct-inlet mass-spectra of heptachlor and 1-hydroxychlordene are shown in Fig. 1A and 2A, respectively.

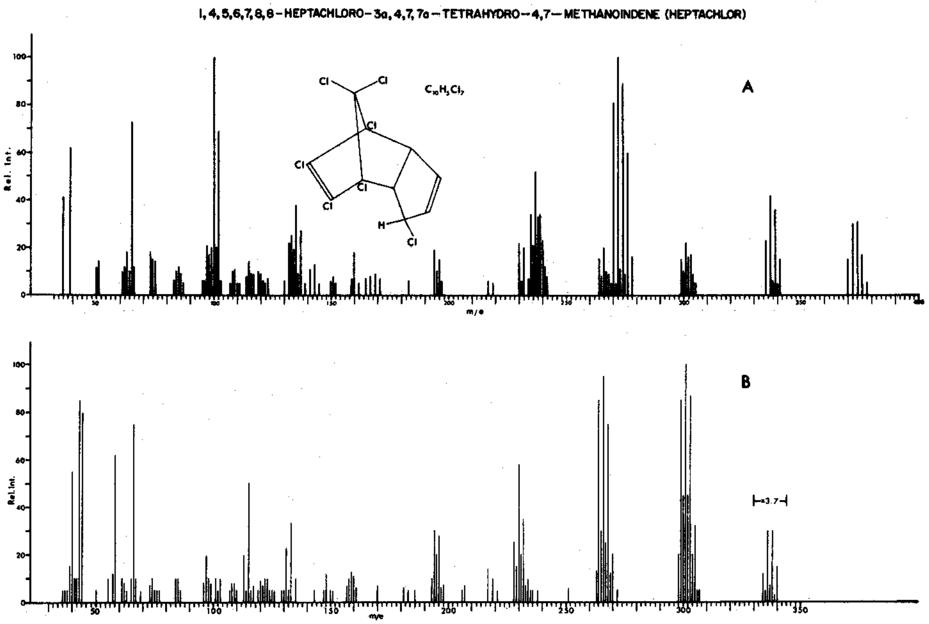


Fig. 1. Mass spectra of heptachlor.
A: direct inlet; B: GC inlet.

The direct inlet spectrum of heptachlor is identical to that published by Damico, Barron and Ruth (1).

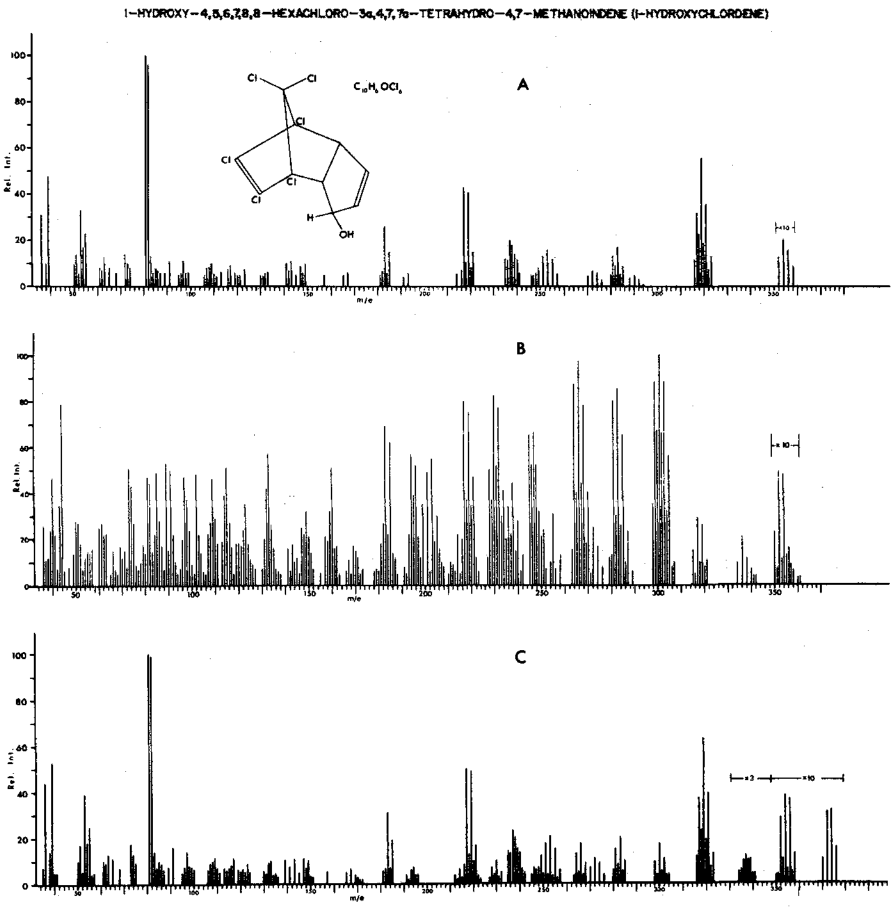
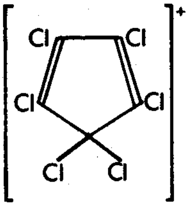
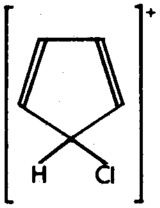
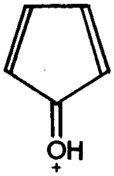
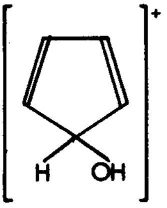


Fig. 2. Mass spectra of 1-hydroxychlordene.
A: direct inlet; B: GC inlet; C: batch inlet.

The major process which seems to occur in the mass spectrometer is a retro-Diels-Alder reaction leading to the formation of ions m/e 270 and 100 in the case of heptachlor, and ions m/e 270, 81, and 82 in the case of 1-hydroxychlordene (1-3).

m/e 270 100 81 82

A second important reaction taking place upon electron impact is the loss of a chlorine atom from the original molecule, leading to the formation of ions m/e 335 and 317 in the case of heptachlor and 1-hydroxychlordene, respectively. The elimination of a HCl molecule is less important, although it is significant in the case of 1-hydroxychlordene (ion at m/e 316).

The molecular ion, M^+, is present in the spectra of both compounds.

Other important ions in the spectra of heptachlor appear at m/e 299 and 300 corresponding to $(M-Cl-HCl)^+$ + $(M-2Cl)^+$, 235 $(C_5Cl_5)^+$, 135 $(C_5H_5Cl_2)^+$, and 65 $(C_5H_5)^+$.

In the spectra of 1-hydroxychlordene other important ions are: m/e 280 + 281, $(M-2HCl)^+$ + $(M-HCl-Cl)^+$, 217 $(C_9H_4Cl_3)^+$, and 183 $(C_9H_3Cl_2)^+$.

The mass spectra obtained through the GC inlet, shown in Fig. 1B and 2B, differ quite drastically from the spectra of the same compounds obtained through the direct inlet system.

In the case of heptachlor, the strong molecular ion present in the direct inlet spectrum (Fig. 1A) is absent in the GC inlet spectrum. The highest ion appears at m/e 334 and corresponds to $(M-HCl)^+$. All other major ions in this spectrum can also be explained by the elimination of chlorine atoms and/or HCl molecules from the original molecule: m/e 298 and 299 correspond to $(M-2HCl)^+$ and $(M-Cl-HCl)^+$, 263 and 264 correspond to $(M-2HCl)^+$ + $(M-HCl-2Cl)^+$, 228 corresponds to $(M-2HCl-2Cl)^+$, and so on. The retro-Diels-Alder reaction, the major process in the direct inlet spectrum, seems to play an almost negligible role in the GC inlet spectrum as shown by the absence of ions at m/e 270 and 100.

The GC inlet spectrum of 1-hydroxychlordene shows some interesting features. The first one is the presence of a m/e 350 ion, which corresponds to a loss of two hydrogen atoms from the original molecule. This suggests that 1-hydroxychlordene is partially converted to 1-ketochlordene, probably in the GC-MS interface. Indeed, some of the major peaks of the GC inlet spectrum of 1-hydroxychlordene are also present in the direct inlet spectrum of 1-ketochlordene (4). These ions appear at m/e 315 and 279 + 280. The remaining major ions can be explained by the elimination of a water molecule, m/e 334 $(M-H_2O)^+$, followed by, or at the same time with, the elimination of chlorine atoms and HCl molecules. Thus, ions m/e 298 and 299 correspond to $(M-H_2O-HCl)^+$ and $(M-H_2O-Cl)^+$, 263 and 264 to $(M-H_2O-HCl-Cl)^+$ and $(M-H_2O-2Cl)^+$, respectively, and so on. Again, as in the case of heptachlor, the retro-Diels-Alder reaction plays an almost negligible role in the GC inlet spectrum of 1-hydroxychlordene.

Under the same GC conditions the gas chromatogram of 1-hydroxychlordene shows only one peak. A mixture of 1-hydroxychlordene and 1-ketochlordene gives two peaks, partially resolved on a 3% OV-17 column, completely resolved on a 3% Dexsil 300 column. This test eliminates the possibility of the conversion of 1-hydroxychlordene to 1-ketochlordene taking place in the GC column.

The mass spectrum of 1-hydroxychlordene introduced through the "batch inlet system" (Fig. 2C) was also obtained. This inlet system subjected the compound to temperature conditions and a path length which were "in-between" the conditions of the direct and GC inlet systems. The spectrum obtained under these "intermediate" conditions is very similar to the spectrum obtained via the GC inlet system. The only interesting difference is the presence of a very weak multiplet starting at m/e 370 with a characteristic "7-chlorine atoms" pattern. This suggests the formation of heptachlor from 1-hydroxychlordene under the conditions present in the batch inlet system.

References

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