

FTIR SPECTROSCOPIC CHARACTERIZATION OF CHLORINATED
CAMPHENES AND BORNENES IN TECHNICAL TOXAPHENEL. Kimmel, G. Leupold, and H. ParlarLehrstuhl für Chemisch-Technische Analyse und Chemische Lebensmitteltechnologie,
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Technical toxaphene is a complex mixture of more than 200 polychlorinated C₁₀-terpenes. It is produced by passing chlorine gas through a solution of camphene of technical quality in carbon tetrachloride under UV-irradiation. The resulting product contains 67-69% chlorine, corresponding to the empirical formula C₁₀H₁₀Cl₈. Due to the lack of selectivity during chlorination, the number of the isomers increases with a nonuniform degree of substitution. An example is the addition of chlorine to the double bond of camphene, which follows an unspecific pathway. This reaction has been the topic of many investigations¹⁻³. Despite contradictory evidence, it has long been accepted that the addition of chlorine to this double bond mainly leads to 2-exo,10-dichlorobornane and, as a minor pathway, to 2-exo,10,10-dichlorobornane, which can be formed via the 8-exo-chlorocamphene by further chlorination. It can be concluded from the formation of these precursors that toxaphene consists mostly of higher substituted chlorobornanes⁴⁻¹¹. On the other hand, the stabilization of the positively charged intermediate by elimination of a proton can also lead to the formation of 10-chlorotricyclene and chlorobornene. These may react either to 6-exo-chlorocamphene via a Wagner-Meerwein rearrangement or to polychlorobornenes or polychlorobornanes, e.g. 2-exo,3-endo,10-trichlorobornene, which, principally, can eliminate HCl and be converted to 2,10-dichlorobornene. Further chlorination of this intermediate can also lead to polychlorobornenes and -camphenes.

Polychlorobornenes were detected by gas chromatography-mass spectrometry¹²⁻¹⁶, although it has long been uncertain whether they are really present in the original mixture or not. Their formation was thought most likely to result from degradation during sample preparation or injection. The same problem existed concerning the origin of chlorocamphenes which have been isolated from irradiated technical toxaphene^{17,18}. Comparisons of the stabilities of various synthetically prepared chlorinated bornane derivatives under elevated temperatures or irradiation have shown that the dehydrohalogenation of toxaphene components results in the formation of polychlorinated camphenes or bornenes^{16, 19, 20}. Therefore, the nature of the unsaturated constituents of toxaphene could be ascertained only by a direct investigation of the technical mixture with a low temperature method. We used liquid chromatography-FTIR-spectroscopy for determining the types and amounts of unsaturated components in technical toxaphene.

Methods and Materials

Material. Camphene, 4,4-DDE, technical toxaphene, the 22-standard mixture, single chlorocamphene standards, and 2,5-endo,6-exo,8,8,9,10-heptachloroborn-2-ene were obtained from Ehrenstorfer, Germany. 2,3-Dichloro or nonsubstituted born-2-ene in pure form were not available commercially, but compounds with similar structure were isolated or prepared in our laboratory as described previously^{16, 16, 21}. All solvents used were of analytical reagent quality.

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Petroleum ether (bp 60-80°C) was purified by distillation.

Column chromatography. Technical toxaphene (5g) was separated into fractions of 15 ml each by column chromatography (length, 1.7 m; i.d., 5 cm; 1150g Silicagel 60, Merck AG-Germany, as adsorbent), and petroleum ether (bp 60-80°C) was used for elution (ca. 1 ml/min, total volume collected 37.5 litre). A total of 2500 fractions was collected with a fraction collector. Each 10th fraction was controlled by FTIR spectroscopy and GC-ECD. Similar fractions were combined to 103 pool fractions which were investigated separately by direct FTIR spectroscopy after evaporation of the solvent and redissolution in 0.5-2.0 ml carbon tetrachloride (CCl₄). Selected pool fractions were also investigated by HRGC-ECNI-MS and HRGC-EI-MS for better characterization. But the results of these measurements were not used for the quantification of unsaturated C₁₀-hydrocarbons in the toxaphene mixture because of possible degradation of these substances during the HRGC-MS measurements. After elution with petroleum ether, the residue on the column, as far as it was extractable, was eluted with 500 ml of methanol.

FTIR spectroscopy. A Nicolet high resolution FTIR 710 spectrometer accompanied by a special work station Nicolet 620 Nicos was used for the infrared measurements. CCl₄ p.a. was used as the solvent.

HRGC-ECD. The HRGC-GC measurements were carried out with a Chrompack 8200. The column used was a DB 5, 60m _ 0.32 mm i.d., film thickness 0.25 µm, and the GC conditions used were as follows: ECD, detector temperature 320°C, make-up gas N₂, 30 ml/min; on-column injector, injection volume 1 µl, temperature program: 120°C (0 min) → 150°C (30°C/min) → 250°C (2 °C/min) (5 min). Assignment of peaks to those of HRGC-MS measurements was achieved with the help of single substance standards as well as by comparison of retention times of the 22-standard mixture on both columns which showed no significant time differences or change of elution order.

GC-ECNI-MS-SIM. The HRGC-ECNI-MS measurements were carried out with a HP 5890 Series II GC that was coupled to a Finnigan 8200 MS. The column used was a DB 5ms, 30m _ 0.25 mm i.d., film thickness 0.25 µm, and the GC conditions used were as follows: carrier gas He 5.0 (Linde), 1.15 ml/min, injection volume 1 µl, injector temperature 230°C, split 1.5 min, split ratio 1:10, transfer line 230°C, interface 230°C, temperature program: 50°C (1 min) → 150°C (70 °C/min) (5 min) → 260°C (2°C/min) (10 min) → 280°C (10 °C/min) (10 min). The MS conditions were as follows: modus: ECNI-SIM, reactand gas: CH₄, ion source pressure: 2.5 _ 10⁻⁴, ion source temperature: 190-200°C, ionization energy: 150 eV, acceleration voltage: 3 kV, resolution 1000.

HRGC-EI-MS. The HRGC-EI-MS measurements were carried out with a HP 5890 Series II GC that was coupled to a Finnigan 8200 MS. The column used was a DB 5ms, 30m _ 0.25 mm i.d., film thickness 0.25 µm, and the GC conditions used were as follows: carrier gas He 5.0 (Linde), 1.15 ml/min, injection volume 1 µl, injector temperature 230°C, split 1.5 min, split ratio 1:10, transfer line 230°C, interface 230°C, temperature program: 50°C (1 min) → 150°C (70 °C/min) (5 min) → 260°C (2°C/min) (10 min) → 280°C (10 °C/min) (10 min). The MS conditions were as follows: ion source temperature: 230°C, ionization energy: 70 eV, mass range: m/z 33-500, resolution: 1000, calibration: perfluorokerosin.

Results and Discussion

Only 4091.4 mg of 5000 mg toxaphene applied could be eluted from the silica gel column.

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The methanol treatment led to an additional desorption of 493.7 mg of toxaphene. That means, ca. 500 mg of toxaphene was still adsorbed on the surface material and can be classified as unextractable, colored, polar components, probably partly polymeric products. This unextractable part has not been considered during the quantification. But it has been assumed that no C10-chloroterpenes were retained on the column because of the high polarity of the unextractable material. The composition of the pool fractions differed widely, as could be seen by GC-ECD. Fractions 1-16 showed only few, well separated peaks, while fractions 17-39 contained more components with a higher degree of overlapping. Fractions 40-103 again contained few, well separated compounds, partly only one main and few minor components. The fractions that had been eluted with methanol could not be investigated by FTIR because of their insolubility in chloroform and CCl_4 .

No FTIR spectra of single unsaturated substances have been obtained during this work because of their low response factors and their low concentrations in the pool fractions. IR spectra of selected model substances formerly isolated after irradiation^{12, 17, 21, 22} have been used for comparison. They show that it is easy to distinguish between chlorobornene and chlorocamphene structures. Chlorobornenes give the typical $>\text{C}=\text{C}<$ absorption band in the region from 1585 to 1600 cm^{-1} , whereas the same absorption band of the chlorocamphenes is shifted to higher wave numbers being located between 1620 and 1655 cm^{-1} . Furthermore, the number of the chlorine atoms at the olefinic carbon atoms can be derived from the $>\text{C}=\text{C}<$ absorption band maxima. Non chlorinated double bond absorptions of chlorobornenes are found at 1585 cm^{-1} , those of mono chlorinated double bonds at 1595-1597 cm^{-1} , and those of dichlorinated double bonds at exactly 1600 cm^{-1} . In the case of chlorocamphenes, typical absorption bands are also existing. The non substituted double bond absorption is registered at 1620 cm^{-1} , that of mono chlorinated double bonds at 1643-1645 cm^{-1} , and that of dichlorinated double bonds at 1655 cm^{-1} .

With FTIR measurements, only the total sum of chlorobornenes and chlorocamphenes, respectively, could be determined. IR absorption of double bonds substituted with different numbers of chlorine are of significantly different intensities, the lowest IR response resulting from non-chlorinated double bonds. Taking the $\nu_{\text{C}=\text{C}}$ intensity of the dichlorinated double bond in cis-chlordane for 100%, that of non-chlorinated double bonds is 10% and that of monochlorinated ones ca. 50% (chlorocamphenes) or ca. 70% (chlorobornenes). The intensities of the vibrations of fully chlorinated $>\text{C}=\text{C}<$ bonds, independent of whether vicinal or axial substituted, are extremely high and lie between 90-105. With the help of the response factors obtained for the standards it was possible to determine the amounts of the chlorobornenes and chlorocamphenes in the pool fractions separated by column chromatography. From the results of the FTIR measurements, a ratio between chlorocamphenes and chlorobornenes of 2.3 was obtained. Evidently, most of the unsaturated compounds in the technical mixture are chlorocamphenes and not chlorobornenes, as has formerly been assumed^{13, 15}. Most of the chlorocamphenes (ca. 75%) belong to a group with a monochlorinated axial double bond. The total amount of congeners with a vicinal dichlorinated double bond is negligible being only 5.6 mg in 5000 mg toxaphene (ca. 0.1%). The reason for this discrimination most likely is the steric hindrance from the chloromethyl- or dichloromethyl groups positioned in the neighbourhood. Chlorocamphenes with an unsubstituted axial double bond in the molecule are also present in considerable amounts in the mixture (0.67%). In the class of chlorobornenes, components with a dichlorinated double bond are the major products. Their total amount is 61.82 mg in 5000 mg toxaphene (1.27%). The formation of these substances during the production of toxaphene is probably controlled by HCl elimination from the ring ($\text{CCl}_2\text{-CHCl}$) of the chlorobornanes which are the dominant

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group in technical toxaphene.

In order to compare the total sum of chlorobornenes and chlorocamphenes obtained by FTIR measurements with the number of compounds in each of these groups of different chlorination degree, quantification of selected fractions by HRGC-EI-MS and HRGC-ECNI-MS was tried, but it was not possible in spite of the high total concentrations of the pool fractions to detect unsaturated compounds after separation. All higher peaks could only be assigned to chlorobornanes.

Acknowledgements

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