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Heterogeneous Hydrodechlorination of Toxaphene

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Toxaphene or Camphechlor is the common name given to an isomeric mixture of camphenes containing from 67 to 69 % chlorine It is prepared by the chlorination of camphene, a bicyclic terpene which is itself prepared from α-pinene. The pesticide is normally considered to have a molecular weight of 414 and an empirical formula of $C_{10}H_{10}Cl_8$ (GUYER et al. 1971, CASIDA et al. 1974) although it is really a complex mixture of chlorinated compounds. It is characterised by a low melting range (70-90° and a low solubility in water (0.5 ppm).

Toxaphene has generally been used as an insecticide in association with DDT as these two compounds have a synergistic effect. The formulation obtained when toxaphene and DDT are combined in the ratio of 2:1 is considerably more toxic to, for example, the bollworm, the tobacco budworm, bollweevils and cotton fleahoppers than either one separately (GUYER et al. 1971). More recently toxaphene has been used in conjunction with methyl-parathion because the use of DDT has been discouraged. However the toxaphene/methyl-parathion mixture is, unlike the DDT formulation, simply additive in its effect on resistant pests.

Toxaphene residues accumulate in the fat of animals either through ingestion or from dermal absorption. The storage level however, is less than that of other chlorinated pesticides, reaching equilibrium very quickly. Elimination of toxaphene from the fat of animals once the input has been stopped is quite rapid. This rapid loss of toxaphene from animal fat facilitates its use for ectoparasite control on livestock providing application is discontinued at least 28 days before slaughter (GUYER et al. 1971). The LD_{50} for toxaphene in rats has been reported as 90 mg kg^{-1} (ANON 1972) which suggests that it should be regarded as 'moderately toxic' (CREMLYN 1979). It is considerably more toxic to fish than mammals (SANBORN et al. 1976). The several components of toxaphene contribute to different extents to its overall toxicity. Two components particularly show superior results (CASIDA et al. 1974). One, a $C_{10}H_{11}Cl_7$ compound, was six times more toxic to mice than technical toxaphene and the other (a $C_{10}H_{10}Cl_8$ compound) was fourteen times more toxic. However technical grade toxaphene contains at least seven major components (OHSAWA et al. 1975).

A variety of procedures have been reported for the determination of toxaphene. Among them are colorimetry (GRAUPNER

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and DUNN 1960), infra-red spectrometry (CLARK 1962) and gas chromatography using an electron caputure detector. The response of toxaphene in a flame ionisation detector is extremely poor. The use of the electron capture detector for the analysis of toxaphene however, causes some special problems. Toxaphene is a complex mutiple component pesticide (HOLMSTEAD et al. 1974) containing in excess of 170 components. The number of peaks observed and the range of retention times over which they are spread is dependent upon the resolution capability of the column used. Hence reliable quantitation of toxaphene presents serious difficulties.

Simplification of the complex structure of technical toxaphene has been attempted using alcoholic potassium hydroxide (ARCHER and CROSBY 1966), (YOUNG et al. 1974) and, by treatment with H_2SO_4 - fuming HNO_3, (KLEIN and LINK 1970). The efficacy of both these procedures has recently been compared with a GC-MS method for the study of toxaphene requiring the monitoring of $m^+/e = 159$, (BOSHOFF and PRETORIUS 1979). The partial dechlorination of toxaphene to yield a simplified chromatogram has also been recently reported (CRIST et al. 1980). We now report our studies on the heterogeneous catalytic hydrodechlorination of toxaphene

MATERIALS AND METHODS

Pye Series 104 gas chromatographs equipped with either a flame ionisation detector (FID) or a Nickel-63 electron capture detector (ECD) were used as required. Columns (2 m x 4 mm i.d.) were packed with 1.5 % OV-17/1.95 % QF-1 on Chromosorb W (silanised), (60-80 mesh) for use with an ECD and either 3 % SE-30 or 5 % OV-101 on Gas Chrom Q (85-100 mesh) for use with an FID.

Palladium and platinum were used as catalyst materials. The support material on which the catalyst was held was chosen to coincide with that of the particular column in use. However the nature of the catalyst support does not appear to affect the performance of the catalyst. To prepare an acid 3 % palladium catalyst palladium chloride (0.15 g) was dissolved in hot glacial acetic acid. To this solution was added the support (5 g) and the resultant mixture evaporated to dryness and dried (110 °, 12 h). For a neutral 3 % palladium catalyst NaOH was added until the mixture was neutral (pH 7.0) and it was then evaporated to dryness. For an alkaline 1 % palladium catalyst palladium chloride (0.05 g) was dissolved in hot glacial acetic acid (50 mL). NaOH (2 g) was added to this solution to neutralise both the acetic acid and the metal salt (calculated as equivalents of HCl). Slight turbidity of the solution suggested the presence of excess hydroxide. Support (5 g) was then added to this solution, followed by evaporation and drying. Platinum catalysts were prepared in a similar manner.

Catalysts were conditioned and activated as previously described (COOKE et al. 1978).

RESULTS AND DISCUSSION

Before the catalytic hydrodechlorination of toxaphene was investigated the behaviour of camphene itself on passage over a heated catalyst was studied. The bicyclic structure of camphene renders it particularly liable to skeletal rearrangement when undergoing reactions. The chromatogram of camphene obtained isothermally (90 °) is presented in Figure 1A. It shows one major and one minor component. The chromatogram shown in Figure 1B was obtained by passage of camphene over a neutral 3 % palladium catalyst (200 °) and clearly contains at least three components. Comparison of retention times suggests that the major peak of the uncatalysed camphene sample corresponds with the first component of the catalysed camphene sample. GC-MS studies on the catalysed camphene sample suggested that the first two components had parent ions at m^+/e = 136 indicative of camphene or camphene-like species. The third peak showed m^+/e = 138 indicative of dihydrocamphene i.e. camphane or similar compound.

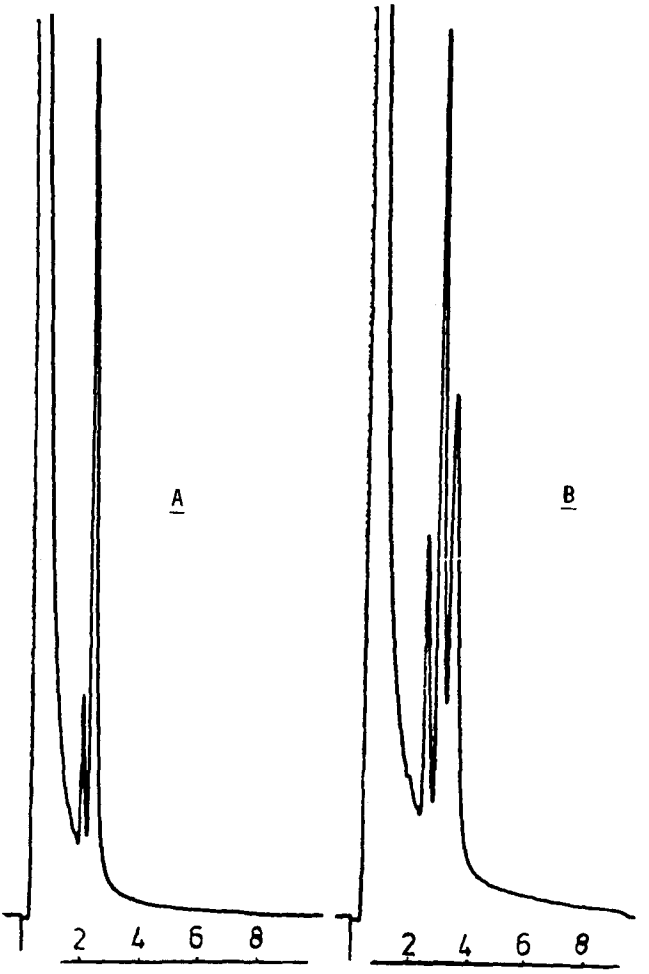
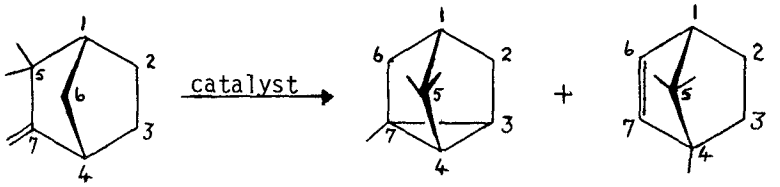


Figure 1

A Chromatogram of camphene (1µg) without catalytic action.

B Chromatogram of camphene after passage over a neutral 3% palladium catalyst (200°).

Camphene is a bicyclic molecule based on the norbornane skeleton. It has been shown (COFFEY 1969) that on a silica/alumina catalyst camphene isomerises to give both tricyclene and bornene.



camphene tricyclene bornene

Titanic acid produces a similar isomerisation which may be characterised as a Wagner-Meerwin rearrangement. Hence the structure of the two components of m^+/e = 136 cannot be definitely assigned. It should be noted that a Wagner-Meerwin type rearrangement involves the acid-catalysed rearrangement of a carbonium ion (usually secondary) to a more stable form (usually tertiary). The hydrocarbon compound with m^+/e = 138 could thus be dihydrocamphene with a methyl group at the C_7 position or dihyrobornene following hydrogenation of the double bond between C_6 and C_7. Hydrogenation of the bond between C_7 and C_3 in tricyclene would yield dihydrocamphene but hydrogenation of the C_7-C_4 bond or the C_4-C_3 bond are possible alternatives. Given this complex situation for the parent hydrocarbon therefore it is not surprising that the hydrodechlorination of toxaphene is neither simple nor easily accomplished.

Several attempts have been made to separate and identify components of toxaphene (HOLMSTEAD et al. 1974 SEIBER et al. 1975). Of the many components identified most would yield as their carbon skeleton the hydrocarbon bornane and only relatively few would yield camphene. Hence structural rearrangement seems to have occurred during the chlorination stage. It is unrealistic therefore to expect a hydrodechlorination reaction to yield camphene as the sole or major product.

The hydrodechlorination of toxaphene achieved by passage over an acidic 3 % palladium catalyst proved difficult to control. At low catalyst temperatures (< 150 ^{o}) little reaction occurred. Above this temperature destruction of the carbon skeleton was apparent. At an optimised catalyst temperature of 220 ^{o} several components eluted shortly after the solvent but prior to the elution time for camphene or related C_{10} species. This observation may well be related to that of Beroza and Sarmiento (1963) who suggested that the HCl formed on reduction of palladium chloride might promote the degradation of the dehalogenated product.

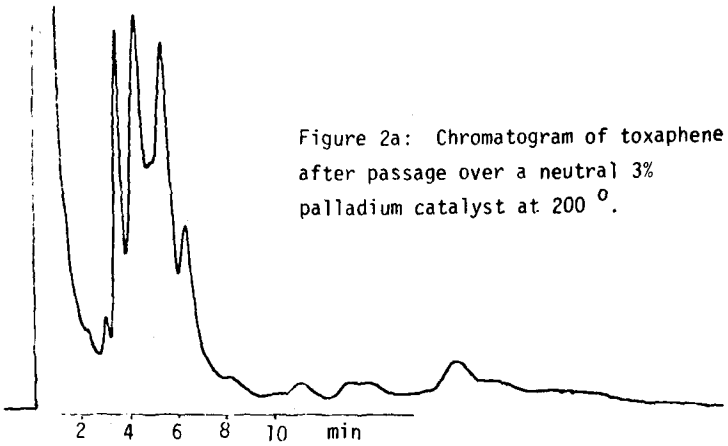


Figure 2a: Chromatogram of toxaphene after passage over a neutral 3% palladium catalyst at 200 °.

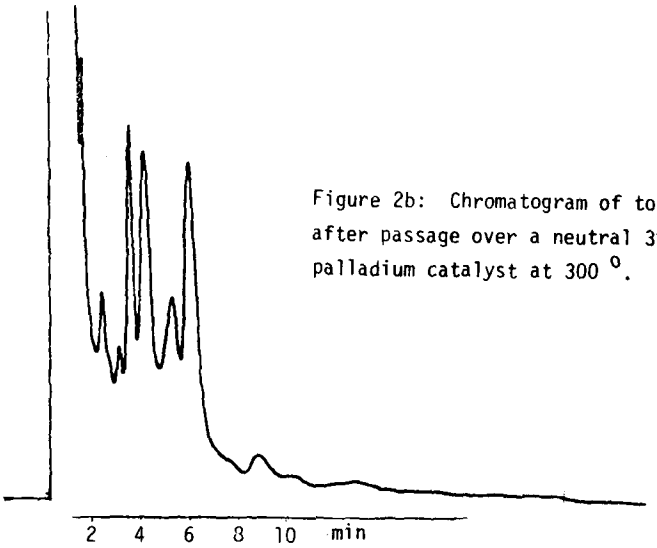


Figure 2b: Chromatogram of toxaphene after passage over a neutral 3% palladium catalyst at 300 °.

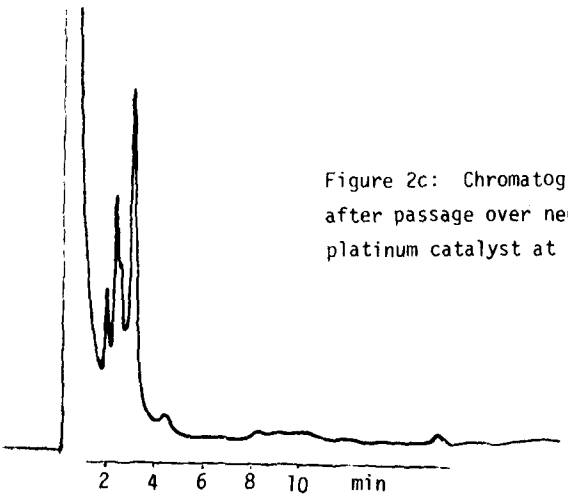


Figure 2c: Chromatogram of toxaphene after passage over neutral 5% platinum catalyst at 190 °.

When a neutral 3 % palladium catalyst was used the optimum temperature again was found to be in the region 200-220 ^{o}. At this temperature four major peaks eluted with short retention times relative to toxaphene (Figure 2a). At higher catalyst temperatures (300 ^{o}) a more complex trace resulted again suggesting some fragmentation of the carbon skeleton (Figure 2b). Although a major proportion of the toxaphene injected on to the catalyst was reduced to hydrocarbon the uneven nature of the baseline indicates that hydrodechlorination was not complete. Subsequent GC-MS studies confirmed that some chlorine-containing compounds were still present.

As both acid and neutral catalysts with a 3 % loading were found to readily degrade the carbon skeleton of toxaphene an alkaline catalyst was prepared with only a 1 % loading. At catalyst temperatures below 150 ^{o} little effect was observed. At temperatures between 175 ^{o} and 220 ^{o} it was apparent that some dechlorination was taking place. The chromatogram obtained displayed only two major peaks, both hydrocarbons (i.e. no chlorines attached). The two major components maximised with respect to the other components at 210-220 ^{o}. Above 220 ^{o} the chromatogram became more complex presumable as skeletal rearrangement and degradation became significant.

The simplest chromatogram obtained for the hydrodechlorination of toxaphene was achieved at 220 ^{o} using a alkaline 1 % palladium catalyst. The possibility of a quantitative response was thus investigated. However no meaningful relationship between peak height and weight injected was found. Attempts were made to quantitate the results obtained when a neutral 3 % palladium catalyst was used. The first five peaks (all chlorine free) were used. However, as increasing weights of toxaphene were injected the third peak increased disproportionately to the others. Further there was no linear relationship between weight injected and detector response. Attempts at using both the sum of the peak heights and peak areas proved unsuccessful.

Experiments carried out using palladium catalysts were repeated using a 5 % platinum catalyst. Under optimum conditions three major components eluted (Figure 2c). GC-MS studies revealed all three to be hydrocarbons with a parent ion at m^{+}/e = 138 for each. The fragmentation patterns for all three were similar with major ions occurring at m^{+}/e = 95 (base peak), 71, 67, 109, and 123. No unsaturated camphene-like compounds were observed. This is probably because the platinum catalysts tend to produce saturated hydrocarbons rather than unsaturated ones (COOKE et al. 1978). The problem of partial dechlorination also occurred with this catalyst.

CONCLUSIONS

Both palladium and platinum catalysts are able to hydrodechlorinate toxaphene to a significant extent. However skeletal degradation occurs before complete reduction is achieved.

Hence no quantitative response was obtained. These problems might be overcome by use of milder catalytic conditions and a longer residence time on the catalyst. However the mild homogeneous catalytic hydrodechlorination reaction developed by COOPER et al. (1979) has relatively little effect upon toxaphene. Unfortunately the reduction of toxaphene by heterogeneous catalysis yields a complex mixture of hydrocarbons due to facile rearrangement of the camphene structure. Prevention of this rearrangement occurring is unlikely and thus quantitation, if achieved will be by measurement of several components. Whilst this is unsatisfactory interference from other organochlorine species is readily avoided if a hydrodechlorination step is used in the analytical procedure for toxaphene.

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