Note

Carbon skeleton capillary gas chromatography

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The simplification of environmental extracts prior to determination of organochlorine pesticide residues is normally attempted via thin-layer or liquid column chromatography[1-4]. However, this procedure is far from satisfactory especially when complex components such as polychlorinated biphenyls and polychlorinated naphthalenes are present[5-7], because the separation achieved is not complete. Simplification of the extract by chemical means rather than by physical separation presents an alternative solution to the problem of interferences. Perchlorination of residues to give decachlorobiphenyl or octachloronaphthalene has recently been reported to provide a much simplified extract for analysis[8,9]. The consequence of perchlorination however, is that the detected species is of higher molecular weight and lower volatility than the precursor compounds necessitating more extreme chromatographic conditions. An alternative to perchlorination is hydrodechlorination, first suggested by Thompson *et al.*[10] and subsequently applied by Asai *et al.*[11] to the determination of organochlorine residues. We have recently used the hydrodechlorination procedure for the routine determination of organochlorine compounds employing gas–solid chromatography[12,13] with packed columns. To prevent interference from other hydrocarbon species a mass spectrometer was used as a selective detector.

The resolution available from capillary columns permits the separation of potential interferents from the compounds of interest. We now report the integration of the micro-catalytic hydrodechlorination reaction with capillary gas chromatography to give carbon skeleton capillary gas chromatography.

EXPERIMENTAL

Reagents

Redistilled hexane was used as the solvent for all standard solutions. Aroclors (Monsanto, Newport, Great Britain), polychlorinated naphthalene (Bayer, Leverkusen, G.F.R.) and Cereclors (ICI, Macclesfield, Great Britain) were used as received. Standard solution concentrations were 10 ppm.

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Apparatus

A Fractovap 2151 Series gas chromatograph (Carlo Erba, Milan, Italy) and splitless injection system fitted with an OV-1 column (25 m × 0.3 mm I.D.) and flame-ionisation detector (FID) was used. The hydrogen carrier gas flow-rate was 2 ml/min with an injection port catalyst temperature of 200–250°. Temperature programme parameters were: 50° hold 3 min; increase 6°/min to 250°; the increase 8°/min to 280°; hold 2 min. Attenuation was × 16.

Catalysts

Catalysts were prepared by published procedures[14] with particular care being taken to neutralise the preparations with 1 *N* sodium hydroxide. Catalysts were then activated using a small oven (see Fig. 3, ref. 15) with a stream of hydrogen and gradual heating to a temperature of 300 °C which was then maintained for at least 2 h. Activated catalysts were then packed into an injection port glass liner (see Fig. 1).
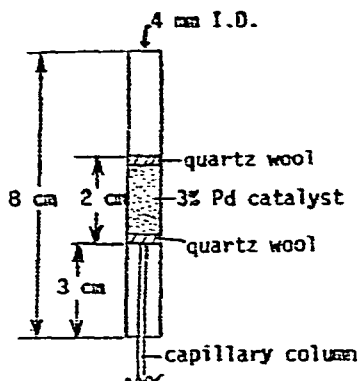

Fig. 1. Injection port liner arrangement for carbon skeleton capillary gas chromatography.

RESULTS AND DISCUSSION

The reactant gas for the dechlorination reaction is hydrogen and consequently this also acts as the carrier gas. The flow of 2 ml/min of hydrogen through the column has no observable effect upon the flame of the ionisation detector. The injection port of the gas chromatographed contains a glass liner some 8 cm long and with an internal diameter of 4 mm. Into the centre of this glass liner is packed the catalyst which is retained in position by quartz wool plugs (Fig. 1). The liner is placed in the injection port and the operating temperature set. Contamination associated with the loading of the catalyst is removed by running the temperature programme through without an injection. Samples may be run without catalysis by removing the liner containing the catalyst and replacing it with an empty one.

We have used this system to study complex mixtures containing polychlorinated biphenyls and polychlorinated naphthalenes. Perhaps more significantly this technique is capable of determing the presence of a polychlorinated alkane residue in a sample. Polychlorinated alkanes are widely used industrially in place of, or in conjunction

with, phthalate esters. Alternative uses are as fire retardants or as lubricating oil additives. They represent a difficult analytical problem because of their multi-component nature. Fig. 2A is the chromatogram of a mixture of organo-chlorine compounds. Although a polychlorinated biphenyl compound, a polychlorinated naph-
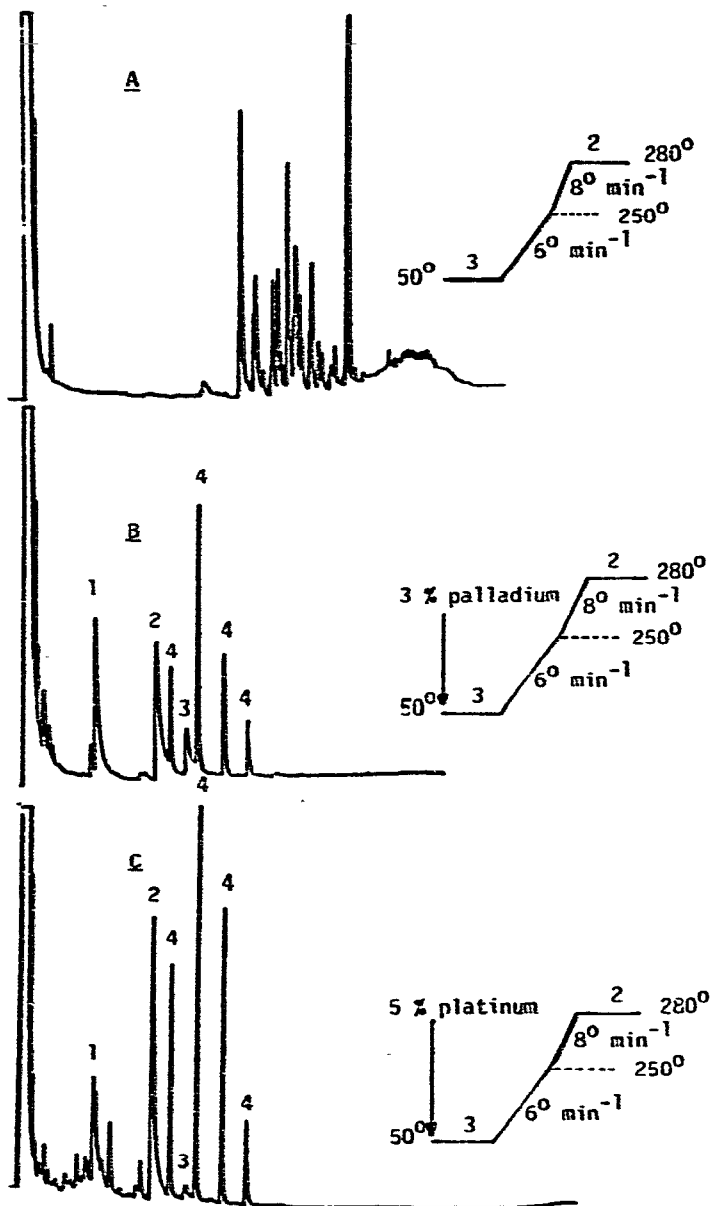

Fig. 2. Gas chromatography–FID of (A) a mixture of a polychlorinated biphenyl, a polychlorinated naphthalene, TDE, and a polychlorinated alkane; (B) the same mixture after catalysis by palladium; (C) the same mixture after catalysis by platinum. 1 = naphthalene; 2 = biphenyl; 3 = diphenylethane; 4 = n-alkanes.

thalene compound, TDE, and a polychlorinated alkane mixture are present in this sample the positive and unambiguous identification of any one of them is a doubtful possibility. Fig. 2B is the chromatogram obtained from the same mixture when a catalyst (3%, palladium) is present in the injection port. Fig. 2C is obtained using a 5% platinum catalyst. Peaks due to biphenyl (1), naphthalene (2), diphenylethane (3) and the hydrocarbon profile of the polychlorinated alkane (4), are well resolved. Peak 3 is due to diphenylethane generated by reduction of TDE.

Comparison of Fig. 2B and C shows, apart from the unsuitability of OV-1 for chromatographing aromatic species (note the tailing peaks), that a platinum catalyst is more suitable for the hydrodechlorination of alkanes and less suitable for the stripping of aromatic species than palladium.

Polychlorinated alkanes are marketed in Great Britain under the tradename "Cereclor". They are made by the chlorination of hydrocarbon fractions. The three different feedstocks used in the production of "Cereclor" are a C_{10}–C_{13} fraction, a C_{14}–C_{17} fraction and a C_{22}–C_{30} fraction. Fig. 3A is a chromatogram of the three basic feedstocks. Fig. 3B is the chromatogram of three Cereclors 50LV, S52 and 54 measured with an FID. A similar trace is obtained using an electron-capture detector. On placing a platinum catalyst in the injection port of the chromatograph and injecting the same three chlorinated alkanes the trace shown in Fig. 3C is obtained. Hydrodechlorination of 50LV gives the C_{10}–C_{13} n-alkanes, of S52 gives the C_{14}–C_{17} n-alkanes. Cereclor 54 gives the C_{22}–C_{30} n-alkanes. Fig. 3D is the capillary gas chromatogram of the hexane extract of a "rubberised" floor tile obtained using an FID. Fig. 3E is the carbon skeleton chromatogram (5% Pt, 200°) of the same extract. The presence of a polychlorinated alkane based upon the C_{14}–C_{17} n-alkane fraction is clearly demonstrated.

We have no evidence to suggest that any "scrambling" reaction leading to the formation of branched-chain alkanes takes place during the catalysis step. The mechanism of this reaction is unclear. Whereas chloro-aromatic species may adsorb onto the catalyst with concommitant formation of an activated complex involving polarization of the carbon–chlorine bond[16], the absence of π-electrons precludes this possibility for alkanes. However, the non-bonding electron pairs on the chlorine atom of the carbon–chlorine bond may become loosely co-ordinated to the catalyst surface. The mechanism depicted in Fig. 4 then becomes a possibility. Scrambling of the alkane chain will occur if the cleavage of the carbon–chlorine bond and formation of the carbon–hydrogen bond are not concerted. Reformation of the transient carbonium ion to a more stable conformation may then occur to give branched-chain alkanes.

The byproduct of the hydrodechlorination is, necessarily, HCl. The fate of this HCl is unclear and attack upon the polymeric silicone liquid phase is a possibility. However, an OV-1 column used with a catalyst and regularly programmed to 300° has degraded no more rapidly than an equivalent column in conventional use.

The activation and conditioning of catalysts for use in capillary gas chromatographs is more critical than for packed columns because a significant amount of volatile material may be displaced from the catalyst during the initial activation. This is particularly true for iron catalysts presumably because of the volatility of ferric chloride. Ideally therefore catalyst material should be activated before being loaded into the injection port to avoid contamination of the top of the column.
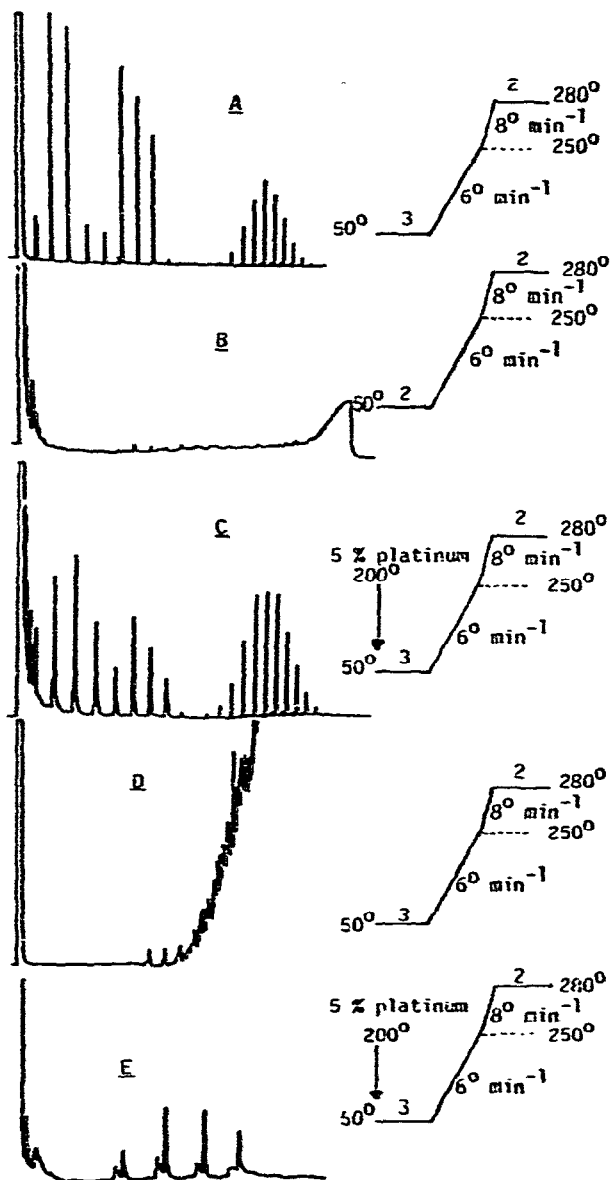
Fig. 3. Gas chromatography–FID of (A) the three Cereclor feedstocks, C_{10}–C_{13}, C_{14}–C_{17}, C_{21}–C_{30}; (B) of the three Cereclors 50LV, S52 and 54; (C) of 50LV, S52 and 54 after catalysis by platinum; and capillary gas chromatography–FID of (D) hexane extract of "rubberised" floor tile; (E) the same extract after catalysis by platinum.

1. Activation of Catalyst

CATALYST SURFACE + H₂ →(ADSORPTION OF HYDROGEN)→

2. Hydrodechlorination, formation of C-H bond

→(ADSORPTION OF C-Cl BOND)→

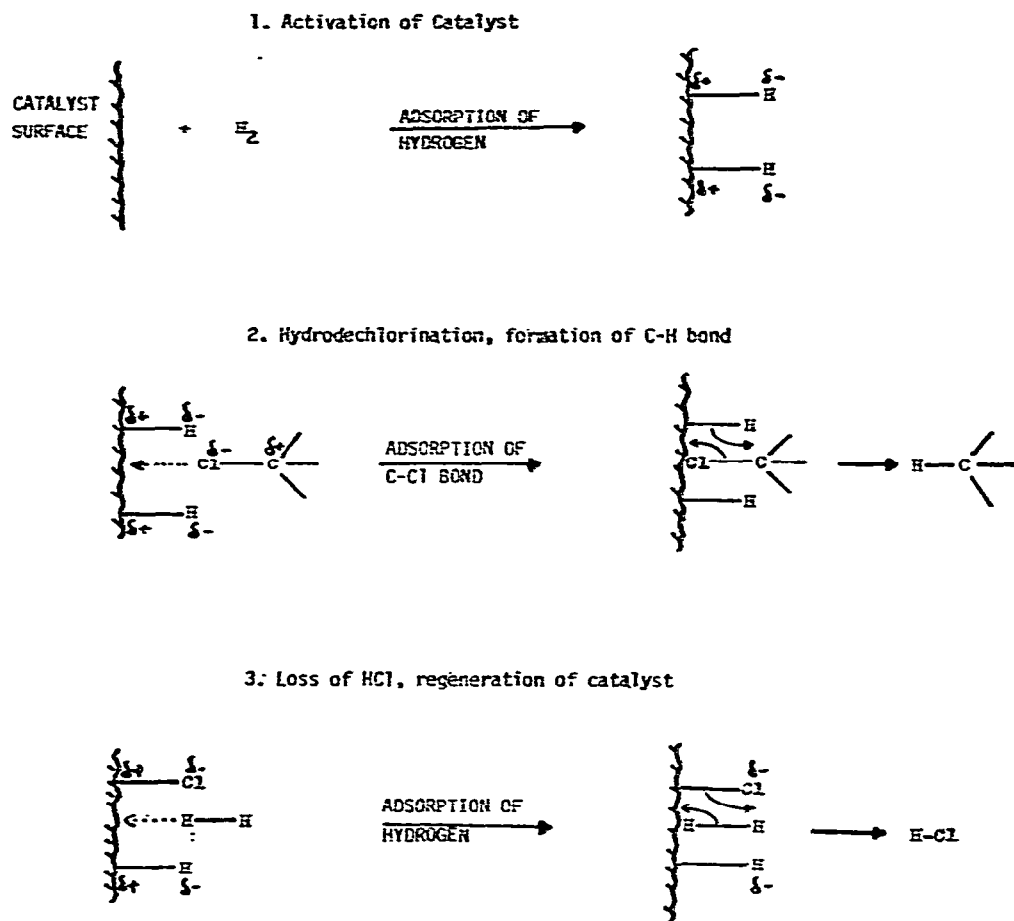3. Loss of HCl, regeneration of catalyst

→(ADSORPTION OF HYDROGEN)→ H-Cl

Fig. 4. A possible mechanism for the catalytic hydrodechlorination of polychlorinated alkanes.

CONCLUSION

The catalytic hydrodechlorination of many environmentally significant organochlorine compounds may be successfully achieved in the injection port of a capillary gas chromatograph, without any apparent effect upon chromatographic performance. For aromatic organochlorine compounds a palladium catalyst is recommended but for polychlorinated alkane compounds a platinum catalyst is preferred.

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