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Polychlorinated Quaterphenyls—A Possible Pathway for Their Formation

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A recent report (KAMPS et al. 1978) deducing the existence of polychlorinated quaterphenyls from chlorine budgeting following analysis of rice oil for a PCB residue has prompted us to report our observations on the existence of the parent hydrocarbon quaterphenyl $C_{24}H_{18}$. We have recently demonstrated (COOKE et al. 1978) that metals such as palladium and platinum may catalyse the hydrodechlorination of polychlorinated biphenyls and polychlorinated naphthalenes. Although the conversion efficiency of these compounds back to their respective parent hydrocarbons was high it was evident that it was not quantitative especially for those PCB mixtures such as Aroclor 1260 which possess a high chlorine content. Although the impure nature of the industrial PCB and PCN products may account for the discrepancy a second possibility exists.

MATERIALS AND METHODS

GC-MS studies were carried out on a Pye Series 104 gas chromatograph interfaced to a V.G. Micromass 16B2 mass spectrometer via a single stage jet separator. Catalytic hydrodechlorination of organochlorine residues was performed by a 3 % palladium catalyst at 300 °C as previously described (COOKE et al. 1978). The mass spectrometer was tuned to detect ions over the mass range m^+/e = 303-308, (P^+, quaterphenyl = 306). The column oven temperature was 280 °C and the column was 2m x 4mm i.d. packed with 2 % RbCl on Chromosorb G. The carrier gas was hydrogen (30 mL min^{-1}).

RESULTS AND DISCUSSION

Injection of 5μL of a 1000 ppm solution of Aroclor 1260 in hexane onto a 3 % palladium catalyst and monitoring of the column effluent at m^+/e = 303-308 revealed the presence of at least five compounds each of which had a significant ion at m^+/e = 306. The mass spectra of each compound displayed the highest weight ion at m^+/e = 306 together with ions corresponding to triphenyl and biphenyl moieties. The ratio of the concentration of biphenyl to triphenyl moieties (as indicated by ion intensity) varied between the various quaterphenyl isomers. Quantitation was difficult but it appeared that about 1-2 % of the weight of Aroclor 1260 injected emerged as quaterphenyl (m^+/e = 306). The presence of polychlorinated quaterphenyls in polychlorinated biphenyls was thus apparently demonstrated. Unfortunately injection of 5μL of a

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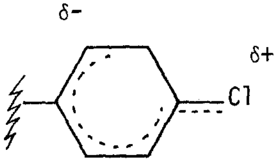
1000 ppm solution of chromatographically homogeneous 1-chlorobiphenyl also yielded the same selection of quaterphenyl isomers after hydrodechlorination. Thus these compounds were being formed by the catalytic reaction rather than being present as impurities in the original PCB mixture. Confirmation of this observation was obtained by injection of a polychlorinated naphthalene compound which gave a small amount of bis-naphthyl ($C_{20}H_{14}$) and of pure 1-chloronaphthalene which also gave bis-naphthyl. Significantly a 3 % iron catalyst also displayed a catalytic capability with regard to hydrodechlorination. However, with an iron catalyst, total dechlorination was not achieved; the residue usually containing from one to three chlorine atoms.

The mechanism of formation of quaterphenyl from biphenyl is complex but quaterphenyl formation is promoted by the presence of a high concentration of PCB on the catalyst indicating a bimolecular coupling reaction analogous to the Wurtz reaction which finds great use in synthetic organic chemistry. Adsorption of an aromatic halide onto a metal catalyst stabilises the resonance form (I) (LAPIERRE et al. 1978). Subsequent attack may be by hydrogen to give biphenyl or by another adsorbed aromatic molecule (if the concentration is sufficiently high) to give a composite aromatic species such as quaterphenyl or bis-naphthyl. Thus the origin of the quaterphenyls which are suggested to exist in rice oils (KAMPS et al. 1978) is now in doubt. Whilst the possibility that these compounds are by-products of the manufacturing process still exists it is also possible that the repeated heating of a PCB (in rice oil for example) in the presence of a metal catalyst (a cooking pot?) causes dimerisation with concommitant elimination of HCl to give polychlorinated quaterphenyls.



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