Pyrolysis and Decomposition Pathways of Alphacypermethrin under Non-Oxidative Conditions

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Abstract

The objective of the work is to understand the decomposition of alphacypermethrin which is one of the most common pyrethroid pesticides, and to examine the formation of pollutants formed during decomposition. This article reports the experimental results of the thermal decomposition of alphacypermethrin under non-oxidative conditions. The experiments were conducted in a tubular reactor at atmospheric pressure. The reaction variables considered were temperature (300-600 °C) and flow rate (27.8-18.2 cm^3/min) which was adjusted to maintain a residence time of 5 s. The pesticide was slowly vaporised at an evaporation rate of 70 μg/min at a temperature of 185°C. The decomposition of alphacypermethrin started around 375 °C and involved an unusual vinylcyclopropane rearrangement-*cum*-aromatisation reaction. At higher temperatures, alphacypermethrin was aromatised into 3-phenoxyphenyl nitrile acetic acid 3-methyl phenyl ester with the concomitant loss of hydrogen chloride molecules. The presence of hydrogen chloride gas was confirmed by FTIR spectroscopy. Other products detected and quantified by GC/MS were *o*-toluic acid, 3-phenoxybenzaldehyde, diphenyl ether, phenoxyphenyl acetonitrile, methyl benzonitrile, phenoxybenzonitrile and phenol. Previous studies carried out on permethrin in our laboratory showed that the process of aromatisation was around 20 kcal/mol lower in energy than the direct rupture of the O-CH_2 linkage for temperatures between 400-1000 °C. The effect of the CN group in alphacypermethrin compared to permethrin was also investigated by density functional theory (DFT) calculations.

Keywords: Pyrolysis, alphacypermethrin, non-oxidative, rearrangement-cum-aromatisation, density functional theory.

1. Introduction

Historically, the preferred technique to treat large amounts of wood for external applications has been to impregnate the timber with chromated copper arsenate (CCA). Although CCA has been substituted with copper boron azole (CBA) or alkaline copper quaternary, the disposal of the waste CCA-treated wood remains a matter of environmental and health concerns, owing to arsenic and chromium (VI) components of the preservative mixture [1-3] and the propensity of the treated timber to form dioxin under fire and smouldering conditions. CCA has been gradually replaced by biocidal organochlorines such as alphacypermethrin, which is representative of a large group of pesticides called pyrethroids. The latter are synthetic forms of the naturally occurring compound pyrethrum [4] which are becoming increasingly used as components in low retention wood preservatives. Their recent rise in popularity is derived from their effectiveness in protecting against Lyctine borers and termites at relatively low concentrations, while exhibiting minimal mammalian toxicity [5]. Most species used in wood protection are halogenated and often contain diphenyl ether moities which are precursors to polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs).

Owing to their extreme toxicity in the environment, PCDD/Fs have been the focus of much scientific, social and technical attention. Dioxins are persistent, bioaccumulative and toxic. They are formed by various ways such as gaseous reactions of precursors. Previous studies showed that wood preservatives increase PCDD/Fs significantly during combustion fires. It was found that forest fires constitute a significant source of dioxins on a global scale, with an emission rate of $1.5 \times 10^{-4} - 6.7 \times 10^{-3}$ mg/kg [6], contributing appreciably to dioxin inventories in some countries, such as Australia.

Despite a great deal of research on the thermal decomposition of pesticides [7-11], the chemical events relating to the formation of toxic gases, PCDD/Fs and their precursors have not yet been experimentally studied in sufficient detail. A detailed understanding of the mechanisms involved during pyrolysis of pyrethroids remains unknown.

Hence, a study of the gas pyrolysis of alphacypermethrin is of assistance in unravelling the complex reaction pathways leading to production of toxic byproducts, possibly including dibenzo-*p*-dioxins and dibenzofurans. Pyrolysis is an ideal technique to use in this study as the complications of reactions involving oxygen and oxygenated radicals are avoided although oxidative reactions must eventually be undertaken.

2. Experimental

2.1 Experimental Apparatus and Procedure

The experimental facility consisted of a gas-feeding system, a gas reaction system and a liquid-gas analysis system as shown in Fig. 1. The pyrolysis experiments were performed in a 75 cm alumina tube reactor, cylindrical in shape with sample placed in the alumina tube, and positioned within a constant-temperature oven held at 185 °C for controlled vaporisation of alphacypermethrin. Nitrogen (99.999%) gas was used as diluent and its flow controlled with a mass flow

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controller. The mixture flowed to a three-zone furnace, each zone controlled independently. The tubular reactor, with a uniform temperature profile (± 5 °C and around 25 cm reaction zone) was used for the decomposition of the alphacypermethrin. A vaporiser and a gas-liquid analysis unit were also included in the system.

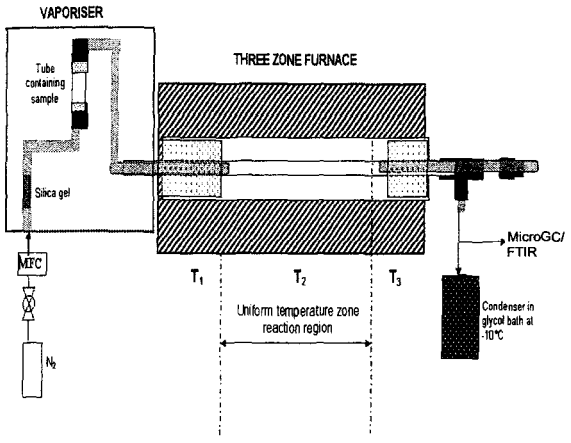


Fig 1: Schematic of experimental facility

Each experiment lasted roughly 90 minutes and involved flowing nitrogen through the reactor over the reactor temperature range of 300 °C-600 °C. The mass of alphacypermethrin sample charged into the reactor was approximately 0.1 g and the evaporation rate was estimated to be 0.07 mg/min. Product gases were trapped in a chilled condenser. After each experiment, the condenser and the alumina tube were rinsed with 1:1 (v/v) solutions of dichloromethane and acetone and then later analysed by GC/MS.

2.2 Analysis

Liquid fraction analyses were performed with a Varian CP-3800 chromatograph equipped with a VF-5ms column. The GC oven temperature program used: 70 °C for 5 min; heating at 10 °C/min to 235 °C held for 10 min and finally heating at 10 °C/min to 280 °C with 5 min hold time. A mass range of m/z 50-500 was examined at a scan rate of 0.5 s per scan. Pyrolysis products were identified by matching the spectra with those from NIST and Varian libraries and by comparing the elution time with authentic standards such as chlorotoluene, methyl benzonitrile, phenol, *o*-toluic acid, acetonitrile-*m*-phenoxy. Analysis of gases included the use of a Varian IR-660 FTIR spectrometer with 0.5 cm^{-1} resolution. The gas cell (Infrared Analysis, USA) has a 10m path length and was flushed three times at least with nitrogen between each analysis.

3. Results and Discussions

3.1 Experimental Measurements

Fig. 2 presents a chromatogram for the pyrolysis of alphacypermethrin at 450 °C, with Table 1 identifying the decomposition products for the experiment. At higher temperatures, more products were obtained.

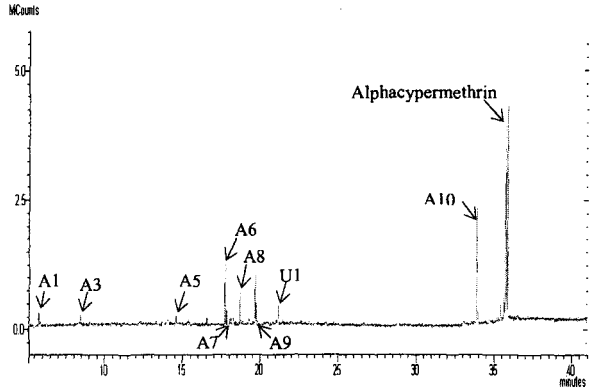
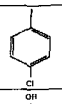
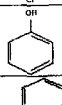
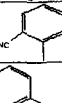
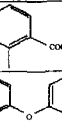
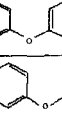
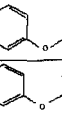
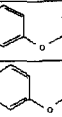
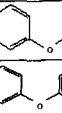
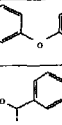
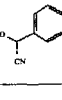


Fig 2: Assignment of peaks in the chromatogram from the analysis of pyrolysis products of alphacypermethrin at 450 °C

At a temperature of 450 °C, 9 compounds were identified, corresponding to in the order of elution 4-chlorotoluene, methyl benzonitrile, diphenyl ether, 3-phenoxybenzaldehyde, phenoxybenzonitrile, phenoxybenzoyl cyanide, phenoxyphenyl acetonitrile, U1 and 3-phenoxyphenyl nitrile acetic acid 3-methyl phenyl ester (A1, A3, A5, A6, A7, A8, A9, U1 and A10 respectively). Based on the mass spectrum, peak U1 was assumed to be 1-methyl 3-phenoxybenzene.

Table 1.0: Identified products generated by pyrolysis of alphacypermethrin for the temperature range of 300 to 600 °C

Peak	Product	Structure	Identification ions m/z (%)	R.T (min)
A1	Chlorotoluene		91 (100), 126 (44)	6.5
A2	Phenol		94 (100), 65 (31)	7.0
A3	Methyl benzonitrile		117 (100), 90 (61), 116 (43), 89 (40)	9.1
A4	o-toluic acid		118 (100), 119 (85), 136 (75), 91 (67)	12.9
A5	Diphenyl ether		170 (100), 141 (52), 115 (50), 51 (37)	14.6
A6	3-phenoxybenzaldehyde		198(100), 169(48), 77(39), 51 (33)	18.3
A7	Phenoxybenzonitrile		195 (100), 194 (50), 77 (46), 51 (45)	18.4
A8	Phenoxybenzoyl cyanide		223 (100), 77 (75), 168 (50)	19.2
A9	Phenoxyphenyl acetonitrile		209 (100), 77 (33), 141 (30)	20.2
A10	3-phenoxyphenyl nitrile acetic acid 3-methyl phenyl ester		119 (100), 91 (14), 343 (13)	27.9

While the source of all peaks can be attributed to thermal decomposition of alphacypermethrin, Peak A10 with m/z ratio of 343 needs more attention. Repeating the experiment at the lower temperature of 375 °C, very small amounts of Peak A10 were observed whilst all other peaks that had been detected at higher temperature (Fig. 2), were absent. This observation suggests that A10, present and is essentially the sole product at the lower temperature, arises from the unimolecular rearrangement of alphacypermethrin. Furthermore, this

observation highlights that this unimolecular pathway is a relatively low energy route, in comparison with the decomposition processes leading to product fragments. The intramolecular rearrangement of alphacypermethrin initially leads to formation of A10 and inhibits the formation of permethrinic acid methyl ester during the pyrolysis of alphacypermethrin. Audino et al. (2002) performed a study of the thermal decomposition of betacypermethrin in the solid state at temperature of 210 °C. Although the study involved the decomposition of betacypermethrin by alkali salts [12], they did observe similar products to the present study including 3-phenoxyphenyl nitrile acetic acid 3-methyl phenyl ester (A10) suggesting a similar initial decomposition reaction for alphacypermethrin. On completion of each experiment, the condensed products were analysed by the GC-MS. Semi-quantitative analysis was based on normalisation of peak areas of the chromatograms over the temperature range of 300 to 600 °C. Product selectivity as a function of major products is presented in Fig. 3 (a-d).

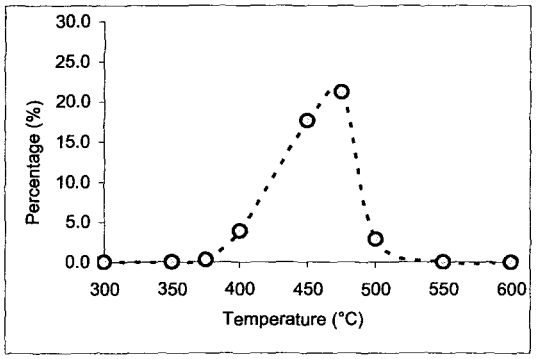


Fig 3 (a): 3-phenoxyphenyl nitrile acetic acid 3-methyl phenyl ester (A10) trend

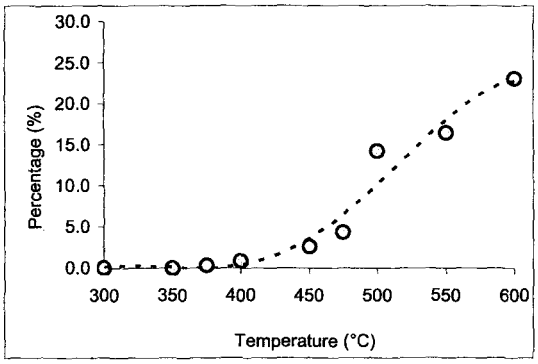


Fig 3 (b): Phenoxyphenylacetonitrile (A9)

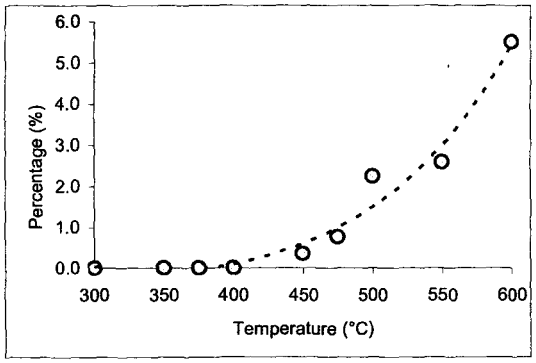


Fig 3 (c): Diphenyl ether (A5) trend

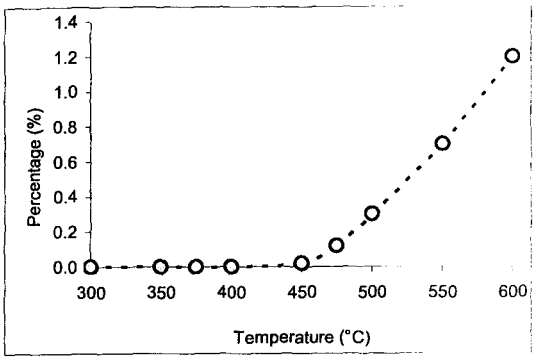


Fig 3 (d): Phenol (A2) trend

Fig.3 (a) shows an interesting trend in the production of the aromatised product from alphacypermethrin. A sharp increase in its concentration is observed up to 450 °C which is followed by a sudden decrease in selectivity reaching zero by 550 °C. In Fig.3 (b), phenoxyphenyl acetonitrile (A9) appears to reach a maximum rate of production at around 600 °C but it is noteworthy to observe that it was detected above around 475 °C, the temperature at which 3-phenoxyphenyl nitrile acetic acid 3-methyl phenyl ester (A10) is decreasing. This is consistent with our proposed pathway. A significant amount of diphenyl ether was also produced as shown in Fig. 3 (c). Somewhat surprisingly, no benzene was identified although it is possible it did condense in the glycol-cooled bath because of its high volatility. Phenol was observed at 475 °C but only in very low concentrations as illustrated in Fig. 3 (d).

3.2 Theoretical Considerations and Pathways

An initial assumption with the thermal decomposition of alphacypermethrin was that reaction would initially take place at the weakest bond in the molecule. The most likely candidate bonds are the O-CHCN bond and the two O-C linkages in the $CNHCC_6H_4$-O-C_6H_5 moiety. Bedekar et al. reported that the thermal rearrangement of dihalogenovinylcyclopropanecaboxylic acids, which constitutes the acid moiety of pyrethroid insecticides, produces a very unusual VCP rearrangement-cum-aromatisation [13]. In the case of permethrin, the aromatisation reaction has been investigated and confirmed [14].

The role of the CN group on O-CHX bond fission in permethrin (X=H) and cypermethrin (X=CN) has been investigated by density functional theory (DFT). Both parent molecules are too large to make detailed quantum chemical calculations so a simpler model has been adopted as shown in Fig.4. This is the species

$HC(=O)OCHXC_6H_5$ (X= H or CN)

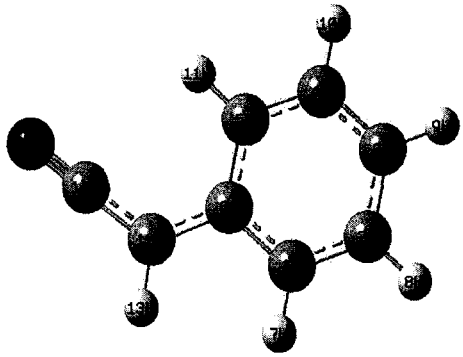


Fig 4: Model structure used in DFT calculation

This model structure has been found to give a good prediction of the O-CH_2 fission in permethrin itself. Bond energies have been calculated at 0 K. There is only a slight temperature correction to 298 K; this correction is lower than the probable absolute error in each bond energy. Bond energies have been evaluated quantum chemically at the B3LYP/6-31G (d) level of theory by optimising the HCOO and $CHXC_6H_5$ structures. For the permethrin model structure, the O-CHX bond energy was found to be 66.1 kcal/mol whereas the bond energy for the cypermethrin model compound was found to be 51.4 kcal/mol. This is a remarkable lowering of the bond energy and is due to the marked stabilisation of the $CH(CN)C_6H_5$ radical compared with the benzyl radical formed in the permethrin model case. The optimised structure in the cyano radical is planar and shows strong resonance stabilisation between the planar N≡CH- group and the ring. The upshot of these calculations is that the activation energy for O-CHCN fission in cypermethrin should be quite similar to the activation energy for internal rearrangement/aromatisation. Hence bond fission in cypermethrin should predominate at a much lower temperature than in permethrin itself.

Fig. 5 shows part of the compound which underwent aromatisation and its mechanism is briefly explained.

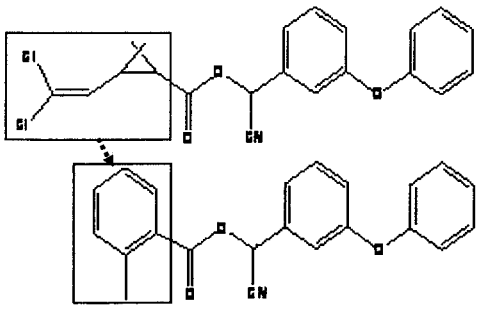


Fig 5: VCP rearrangement in alphacypermethrin

The first step corresponds to hydrogen migration from one of the two methyl groups to the carbon bearing the chlorine atoms. Subsequent steps involve chlorine shift, hydrogen chloride elimination, cyclisation and a second hydrogen chloride elimination to eventually form the acetonitrile ester of *o*-toluic acid.

This explains why A10 was observed at 375 °C, prior to the formation of other compounds that arose from the O-CH_2 bond. In addition, no products were obtained from the rupture of the O-CH_2 linkage of the dichlorovinylcyclopropane carboxylic acid ester. Moreover, when FTIR gas analysis was carried out at this temperature, HCl was observed in the FTIR spectrum, consistent with the mechanism.

4. Conclusions

Although no dibenzofuran was observed at 600 °C, precursors such as diphenyl ether (A5) and phenol (A2) were identified. Fission of the ether bridge in A5 can produce phenyl and phenoxy radicals, which are usually well known to be direct precursors for PCDD/Fs. The aromatisation and concomitant loss of HCl was the predominant initial reaction for alphacypermethrin and chlorine was converted to this relatively poor chlorinating agent. This could explain why PCDD/Fs were not detected in these experiments. In our future studies, oxygen and chlorinating agents such as copper chloride will be used to determine if these facilitate PCDD/Fs formation.

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6. References

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