

# Thermal Decomposition of Chlorpyrifos - an Experimental Investigation

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## Abstract

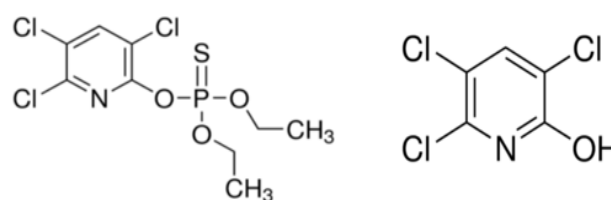
Organophosphate compounds are a group of chemicals that are commonly used in pest control. One widely used organophosphate is chlorpyrifos (CPF), which has been associated with acetylcholinesterase inhibition (AChE), an acute neurotoxin. Further, under thermal decomposition conditions, such as those that occur in bushfires, CPF has been shown to produce a dioxin-like compound 2,3,7,8-tetrachloro-[1,4]-dioxinodipyridine (TCDDpy). To assist in understanding the reaction of CPF, an experimental methodology was developed which enabled the study of its thermal decomposition. CPF was pyrolysed in a three-zone furnace, leading to the formation of its major degradation product, 3,5,6-trichloro-2-pyridinol (TCP). The study revealed that ethylene gas and a solid sulfur/phosphorous compound were also generated with the TCP product. TCP undergoes further thermal decomposition to form several chlorinated products. Experiments undertaken under oxidative conditions revealed that TCP (at temperatures above 900 K and at a residence time of 9 s) also produced HCl and cis and trans forms of TCDDpy. The results of this study compare favourably with our previous theoretical work.

**Keywords:** Chlorpyrifos, Thermal Decomposition, Kinetics, Pyrolysis, Oxidative

## 1. Introduction

Organophosphate pesticides were introduced as an alternative to organochloride pesticides. The organophosphate compounds offer a stable product that is used for pest control. Specifically, Chlorpyrifos (O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate, CAS: 2921-88-2) (CPF) is known for combating a wide range of pests and is one of the most widely used of all pesticides. Recently, the U.S. federal appeals court ordered the U.S. Environmental Protection Agency (EPA) to ban all sales of CPF due to the neurodevelopmental damage to children. CPF persists in soil with a long half-life (that varies between each soil type) and can persist in the environment from 14 days to 1 year (Howard, 1991). As CPF still has such a notorious presence in the environment, the impact of CPF needs to be further investigated. Whilst there is information on the environmental fate of CPF, very little is known about the impacts of fire or heat on CPF. Sakiyama et al. and

Moriwakie et al. studied the thermal decomposition and noted that CPF undergoes the thermal elimination of phosphate and forms the 2,3,7,8-tetrachloro-[1,4]-dioxinodipyridine (TCDDpy) molecule. The TCDDpy molecule is a nitrogen analogue of the extremely toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin (Moriwaki et al., 2013; Sakiyama, Weber, Behnisch, & Nakano, 2012). Most recently, we developed a potential energy surface (PES) for CPF, TCP and TCDDpy based on quantum chemical techniques. The analysis disclosed two key mechanisms that represent the primary pathways associated with thermal decomposition of CPF. The first pathway involves the production of the TCP molecule from CPF and the second describes the complex steps involved with the formation of TCDDpy from the TCP molecule (Kennedy & Mackie, 2018). Apart from these studies, very little information is available on the thermal decomposition of CPF, especially from the experimental perspective. The molecular structures of both CPF and the degradation product 3,5,6-trichloro-3-pyridinol (TCP) are illustrated in Figure 1.



**Figure 1.** Structure of CPF (left) and its degradation product TCP (right).

## 2. Methodology

The experimental design was based on the flow of gaseous CPF through a reactor using a three-zone furnace. The three-zone furnace was configured to allow a vaporiser zone (104 °C) and a reactor zone, with an operating range between 550 to 850 °C. An alumina tube (6 mm od) was placed inside the furnace to allow passage of the flow of N<sub>2</sub> or air through each zone. A fully charged container of 100 mg of solid CPF was then placed in the vaporiser zone of the furnace where the vaporised CPF was flowing into the reactor zone at residence times of between 10 to 90 s. An FT-IR (Perkin Elmer Spectrum 100, 11 cm path length Teflon gas cell fitted with 25 x 5 mm KBr windows) was used to detect

gaseous products. A Shimadzu GCMS-QP5000 (Plot-Q column 30 m x 0.32 mm) and Agilent GC 6890 MS 5973N (HP-5MS column 30 m x 0.25 mm) were used to analyse the gas and soluble solid/liquid products, respectively.

### 3. Results and Discussion

#### 3.1 Pyrolysis of chlorpyrifos

The pyrolysis of CPF (in N<sub>2</sub>) revealed two distinct decomposition stages. The first stage occurs at temperatures below 650 °C, where the CPF molecule decomposes to form TCP, with the concomitant release of two ethylene molecules. In the second stage, at temperatures above 650 °C, the breakdown of CPF occurs along with the decomposition of the TCP product. The low temperature decomposition of CPF was examined between 550 °C and 650 °C. Between these temperature ranges, the formation of two major products was observed. The first significant product was ethylene gas, that is the primary product found in the vapour phase, as illustrated in the black trace in Figure 2. The second major product was a grey/white solid that was recovered from the alumina tube and the exit PFA tubing. The solid product that formed was confirmed to be TCP and 2,3,5-Trichloropyridine by GC/MS analysis. The formation of ethylene supports the hypothesis that the CPF molecule will undergo hydrogen radical transfer, leading to the generation of two molecules of ethylene per molecule of CPF. A highly viscous brown residue was found to be deposited in the reactor. The elemental composition of this residue was analysed by ICPOES, confirming the presence of sulfur and phosphorous, related to the HOPOS present in CPF. Currently, there is minimal information on the HOPOS which is not listed in SciFinder Scholar. Recent theoretical work predicts that the breakage of the HOPOS from CPF will mostly likely form a trimer similar to metaphosphoric acid. At temperatures exceeding 650 °C, a secondary mechanism was observed. Both CO and as of yet an unidentified nitrogen heteroaromatic species was formed, as observed by FTIR as shown in blue in Figure 2. The production of both CO and nitrogen heteroaromatic was also predicted by theoretical work on the pyrolysis of TCP. When TCP undergoes thermal decomposition, the rotation of O-H group occurs through phenolic H transfer forming trichlorinated 3H-pyrrole and the release of a CO molecule. The presence of a compound such as trichlorinated 3H-pyrrole, could lead to the formation of short chained nitrogen chlorinated molecules such as cyanogen chloride and chlorinated crotonitrile.

#### 3.2 Kinetic analysis

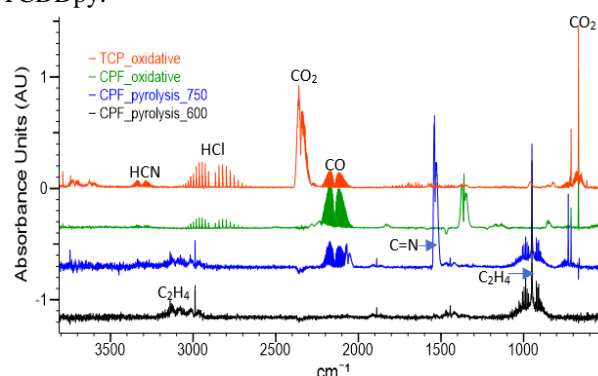
Kinetic analysis was undertaken for the first order reaction of the pyrolysis of CPF between the temperatures of 500 to 650 °C. Results are presented in Table I. The isothermal analysis was undertaken at three temperatures of 500, 600 and 650 °C and temperature programmed kinetic analysis was undertaken between 500 °C and 650 °C with a ramp of 6 °C/min.

**Table 1.** Activation energy for isothermal and non-isothermal.

Condition	E <sub>a</sub> (kJ/mol)	A (s <sup>-1</sup> )
Isothermal	102±2	1.57x10 <sup>3</sup> ±50
Programmed analysis	114±4	5.76x10 <sup>5</sup> ±3x10 <sup>3</sup>

#### 3.3 Reaction of chlorpyrifos under oxidative conditions

Switching of the carrier gas of N<sub>2</sub> to air bath gas enabled the study of the decomposition of CPF to be examined under oxidative conditions. The oxidative reactions were examined at temperatures between 630 to 830 °C and residence times of 8 to 50 s. The resulting FT-IR spectrum confirmed the presence of the key species HCl, as predicted in the formation of TCDDpy in our previous theoretical work. Other products such as hydrogen cyanide and both CO<sub>2</sub> and CO were also detected. Similar experimental conditions were also completed on TCP revealing comparable results; however, higher concentrations of HCl and hydrogen cyanide absorption were observed, as seen in the orange trace in Figure 2. This implies that CPF initially decomposed to TCP, and the TCP subsequently decomposed into products such as TCDDpy.



**Figure 2.** FT-IR spectrum of gas phase pyrolysis (black and blue) and oxidative (orange and green) products.

### References

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