



## Formation of chlorobenzenes by oxidative thermal decomposition of 1,3-dichloropropene



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### ABSTRACT

We combine combustion experiments and density functional theory (DFT) calculations to investigate the formation of chlorobenzenes from oxidative thermal decomposition of 1,3-dichloropropene. Mono- to hexa-chlorobenzenes are observed between 800 and 1150 K, and the extent of chlorination was proportional to the combustion temperature. Higher chlorinated congeners of chlorobenzene (tetra-, penta-, hexa-chlorobenzene) are only observed in trace amounts between 950 and 1050 K. DFT calculations indicate that cyclisation of chlorinated hexatrienes proceeds via open-shell radical pathways. These species represent key components in the formation mechanism of chlorinated polyaromatic hydrocarbons. Results presented herein should provide better understanding of the evolution of soot from combustion/pyrolysis of short chlorinated alkenes.

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### 1. Introduction

1,3-Dichloropropene (1,3-D) is used extensively in agriculture as a pre-plant soil-fumigant primarily for the control of parasites and soil-borne bacteria and viruses. 1,3-D was first introduced in 1956 and is now widely used in many countries, including the USA, Canada, Australia and the European Union (where it is currently being phased out). The extensive use of pesticides has stimulated research aimed at understanding the chemical mechanism and products of their combustion [1–3]. These products can include highly toxic species, such as dioxins and their precursors. While a number of investigations have focused on toxicity of 1,3-D [4–6], the mechanism(s) and products of its combustion have not yet been reported.

Thermal decomposition of chlorinated alkanes and alkenes typically results in chlorinated aromatic pollutants. Precursors of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) have been observed during the heterogeneous oxidative/pyrolytic decomposition of chloroaliphatic hydrocarbons [7]. Similarly, chloroaromatic compounds and their precursors have been detected during the decomposition of chlorinated short-chain aliphatic hydrocarbons [7–23]. The latter investigations show that formation of PCDD/F precursors proceeds *via* molecular growth

reactions triggered by alkyl and chlorinated vinyl radicals [16,21,22] *via* rearrangement and radical recombination between unsaturated intermediates [9].

Benzene and chlorobenzenes have also been identified and quantified in the combustion of chlorinated short-chain hydrocarbons [15,23]. The formation of these chloroaromatic compounds has been attributed to *de novo* processes enabled by soot particles in the flame in addition to coupling of gas phase precursors. High yields of hexachlorobenzene were observed during fly ash-catalysed combustion of trichloroethylene [12]. This supports the theory that chloroaromatic compounds can be formed in the high-temperature post combustion zone, which provides the precursors necessary for PCDD/F formation in lower temperature zones. Similarly, hexachlorobenzene was observed during the pyrolysis of hexachloropropene above 773 K, *via* self-recombination of C<sub>3</sub>Cl<sub>5</sub> radicals [19]. These radicals are produced during the initial decomposition of hexachloropropene (C<sub>3</sub>Cl<sub>6</sub>). It is also possible for chlorine atoms to recombine with propene or any available radical to form the trichloropropargyl radical, which can self-recombine to produce chlorinated benzenes. Pyrolysis of trichloroethene above 1000 K has also been observed to yield hexachlorobenzene [21].

In this work, we investigate formation of chlorobenzenes, *via* high-temperature combustion of 1,3-D using a combined experimental and quantum chemical approach. Chlorobenzenes have been categorised by the International Agency for Research on

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Cancer (IARC) as a Group 2B animal carcinogen and a potential human carcinogen, and in addition they are precursors of PCDD/Fs [8,17,18]. Experiments show that between 650 and 1050 K, combustion products of 1,3-D include mono- to hexa-chlorinated benzenes. Quantum chemical calculations of reaction pathways reveal that these products can form via a number of alternate cyclisation pathways. The most thermodynamically and kinetically favourable pathways are observed to be propagated by perchlorohexatriene-derived radicals. Kinetic and thermodynamic parameters presented here will be useful for future kinetic models of halohydrocarbon combustion. Formation of the first chlorinated aromatic ring typically initiates the formation of chlorinated polycyclic aromatic hydrocarbons (PAHs). Results from this study will also contribute toward a better understanding of the formation of soot during combustion of chlorinated short-chain hydrocarbons.

## 2. Methods

### 2.1. Experimental

The experimental apparatus employed in the thermal decomposition of 1,3-D is illustrated in Fig. 1.

1,3-D (98%, Dow Agroscience, Australia), a faint yellow liquid at room temperature, was introduced into the system using a syringe pump operated at a constant rate to keep the reactant concentration at 8580 ppm, in a dilute stream of air in nitrogen (6% O<sub>2</sub>). We used a heating tape (set at 403 K) to ensure proper vaporisation of the reactant prior to entering the reactor and also minimise temperature gradients inside the reactor. The resulting vapour/nitrogen mixture entrained a controlled amount of oxygen, with oxygen concentration monitored on the molecular sieve channel 1 of a 490 micro gas chromatograph (Agilent, USA). We used the molecular sieve and Poraplot Q columns of the same micro GC to measure the CO and CO<sub>2</sub> produced during the experiment with the micro GC calibrated with a gas standard. The chloride ion obtained from NaOH trap was analysed using Dionex DX-100 ion

chromatograph. We used drierite to remove the water vapour prior to product analyses in order to avoid damage to our analytic instruments.

The jet stirred reactor (JSR) used here consists of a sphere (54 mm i.d., 82.3 cm<sup>3</sup> in volume), made of quartz (99.99% purity to minimise wall catalytic reactions). The spherical part of the reactor is equipped with four nozzles each of 3 mm i.d. for the injection of the feed gas and reactant vapour thereby obtaining the stirring. The reactor is aligned along the centreline of an electrically heated single-zone furnace (Brother furnace China) calibrated from 623 K to 1123 K with a thermocouple placed along the tube to define a uniform temperature zone. The tail end of the reactor was connected to different product collection systems.

Once the temperature and reactor conditions are stabilised, reactants are introduced into the reactor via the syringe pump at a steady state and product sampling from the reactor commences immediately. The experiments were carried out over a wide temperature range of 673–1073 K with an equivalence ratio of 0.5. For all experiments, the pressure was 1 atm and the residence time was 10 s. Sampling of reactants, stable intermediates and products from the reactor lasted for 3 h in each run. The polytetrafluoroethylene connection tubes are normally rinsed with dichloromethane and/or hexane solution to recover adsorbed products and to avoid contamination of succeeding runs. We used a glass tube loaded with 200 mg of XAD-2 resin (Supelpak-2, Sigma-Aldrich, Australia) and connected it at the reactor outlet as our VOC trap. Hexane and dichloromethane (DCM) solvent trap was chilled in a cold glycol bath (273 K) to collect any condensable products.

Products were analysed with GC–MS. We adapted the general procedures of the National Institute for Occupational Safety and Health (NIOSH) method 1003. We used XAD-2 resin (in place of activated charcoal) as the adsorbent and *n*-hexane (instead of CS<sub>2</sub>) as the solvent. After each experiment, the used XAD-2 resin was collected and sonicated with 40 mL hexane for 2 h. The XAD-2 extract was filtered and injected (split ratio 10:1) into the Agilent 7890 GC and 7200 Accurate-mass Q-TOF GC/MS with a

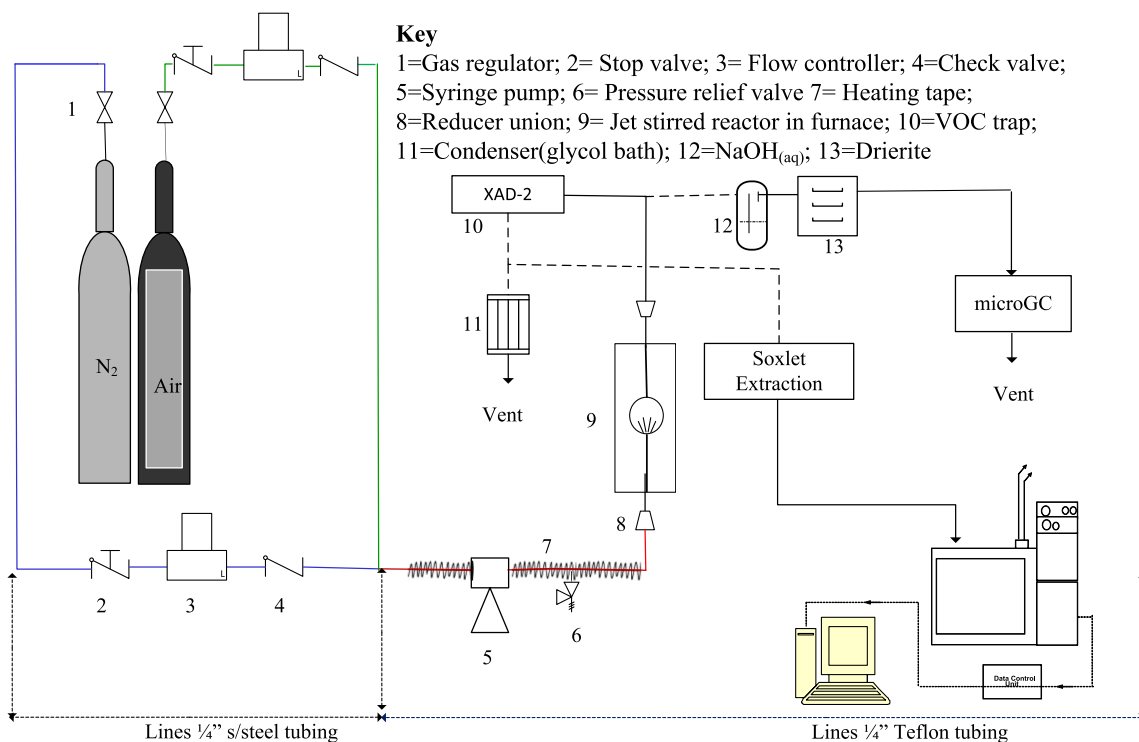


Fig. 1. Schematic of the experimental set-up.

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