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FORMATION OF TOXIC SPECIES IN OXIDATION OF 4-CHLOROTHIOPHENOL

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Introduction

Chlorinated thiophenols (CTP) constitute a group of the most important precursors for the formation of polychlorinated dibenzothiophene (PCDT) and polychlorinated thianthrene (PCTA). PCDT/TA are environmentally and toxicologically interesting compounds due to their structural similarity with their oxygenated counterparts i-e polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF). Owing to their resistance to metabolise and chemical degradation and their lipophilic character, PCDT/TA have potential to accumulate in the food chain; especially in fish and other marine organisms[1]. A number of studies have also documented the negative effects of sulfur containing volatile organic compounds (VOC) on human health, such as CTP displaying carcinogenic health effects[2] and benzothiophenes and naphthalene thiols having the potency to cause acute toxicity[3]. Over the last four decades, a great deal of research has been undertaken on the formation of PCDD/F from various precursors and under different operational conditions. However, there are no experimental investigations on the potential for CTP to form PCDT/TA, possibly hindered by the absence of PCDT/TA standards for quantification[4]. High correlation between PCDT/TA and PCDD/F concentrations suggests similar governing mechanisms of formation in thermal systems[5]. In our previous theoretical study[2], we constructed reaction pathways operating in the formation of PCDT/TA, and reported relevant thermochemical and kinetic parameters. This study reports the results of experimental and quantum chemical investigations on the thermal degradation of 4-chlorothiophenol (4-CTP) under oxidative conditions for a reaction time of 2s over the temperature range of 300-800 ^{o}C. Furthermore pathways for the formation of important VOC, not previously reported in literature are also proposed.

Methods

A laboratory-scale apparatus consisted of reactant vaporizer, a tubular quartz reactor and a sample collecting system. To avoid surface effects quartz reactor was coated with boric acid[6]. 4-CTP vapors were diluted in nitrogen flow and mixed with controlled amount of oxygen to result in fuel equivalence ratio of 0.011. Two high purity quartz rods (9.5 mm o.d.) were inserted into both ends of the reactor to enable modification of reactor volume, to force the reactants and products flow in annular space to minimize decomposition in lower temperature region and to maintain same residence time for all experiments carried out at different temperatures. A XAD-2 resin cartridge was installed after the reactor tube to trap all PCDT/TA and VOC products. Gas chromatography - quadruple time of flight mass spectrometry (GC-QTOFMS) (Agilent, Australia) operating in split mode (1:10), served to identify VOC and PCDT/TA products. The GC oven housed a HP-5MS column (30 m × 0.25 mm i.d. × 0.25 μm). Helium was used as the carrier gas flowing at a constant rate of 1.2 cm^3/min. The injector operated at 250 ^{o}C and the temperature program was started from 40 ^{o}C, held for 2 min, and then increased at a temperature ramp of 10 ^{o}C/min to 295 ^{o}C and held for 1 min. The electron impact source functioned at an ionization energy of 70 eV. Both the source and transfer line were maintained at 240 ^{o}C. We adapted the general procedures of National Institute for Occupational Safety and Health (NIOSH) method 1003 for analysis of products. The eluted peaks were identified by matching their mass spectra with those from the NIST library, GC retention times and from genuine standards.

Gaussian suite[7] of programs was used to perform computations at the M062X/6-311+G(d,p)[8] level of theory. Transition structures were linked to their reactants and products via calculations of intrinsic reaction coordinate (IRC).

Results and discussion

Experimental results indicate the formation of mono-diCDT including 2,8-dichlorodibenzothiophene (2,8-DCDT), 2,7-DCDT and 2-monochlorodibenzothiophene (2-MCDT). Fig. 1 presents the formation of the main PCDT isomers as a function of temperature during oxidation of 4-CTP. Mechanism for the formation of these compounds are presented in our previous study2. However results also indicate

the formation of PCDF in excess of 500 °C with 2,8-dichlorodibenzofuran (2,8-DCDF) being the most abundant followed by 2-monochlorodibenzofuran (2-MCDF), 2,7-DCDF and minor quantity of dibenzofuran (DF). It is evident from Fig. 1 that we observed no isomers of PCDD or PCTA and our observations are in agreement with previous research work, according to which ortho substitution of Cl is essential in the precursor for the formation of dioxins and its like compounds[9]. The identification of the PCDF and PCDT congeners were based on the injection of genuine standards and comparison of the retention times (see Fig. 1(b)).

Fig. 2 presents the main VOC species formed in the thermal oxidation of 4-CTP for experiment conducted at 650 °C. It is obvious from Fig. 2 that 4-chlorophenol (4-CP) was a major product; most likely formed as a result of substitution of SH group by an OH group. 4-CP served as a building block for the detected PCDFs isomers. Sulfur VOC identified in the system, included 4-chlorobenzothiophene (CBT), 7-chloronaphthalene thiol (CNT) and 2,8-dichlorodiphenyl sulfide. Other identified products included 4-chlorobenzaldehyde, 2,4-dichlorophenol, 2-methyl benzofuran, 4-chloro-2-methyl benzofuran, 2-chloronaphthalene and 2,4-dichloro-2-methyl benzofuran.

Fig. 3 illustrates the formation pathways for two important VOC (CBT and CNT) in the oxidation of 4-CTP. Chlorocyclopentadiene (C_5H_4Cl) acts as an important precursor for the formation of several dominant experimental products in system is formed via decomposition of 4-chlorothiophenoxy. A thiophenoxy radical forms in the decomposition of thiophenol molecule either by unimolecular elimination or through bimolecular ions with H/OH radical pool.

Formation of C_5H_4Cl involves ring contraction of chlorothiophenoxy radical into mesomer M1 via a high energy barrier of 65.3 kcal/mol, which isomerizes further into intermediate M2 followed by subsequent loss of CS moiety and formation of resonance stabilized radical C_5H_4Cl. Coupling of 4-CTP and C_5H_4Cl at radical site of latter produces M3 with a reaction barrier of 17.3 kcal/mol and an endothermicity of 9.9 kcal/mol. M3 further eliminates HCl to produce M4. This elimination step is associated with a modest endothermicity of 10.8 kcal/mol. Under oxidative condition, $^3\Sigma_g O$ adds at the radical site forming a peroxy-type radical (M5). Barrierless direct scission of the O-O bond in M6 is predicted to be endoergic by 56.9 kcal/mol. This results in the generation of the high energy moiety M7 via a small activation enthalpy of 6.5 kcal/mol. Ring opening occurs via 1,2-hydrogen shift and produce M8. In the subsequent step, a CO molecule is eliminated providing M9 via barrier of 34.6 kcal/mol, via TS7, providing intermediate M9 Next, C_2H_2 is eliminated from the M10 adduct by overcoming a sizable activation barrier of 43.3 kcal/mol. The formation of M8 and C_2H_2 is endoergic by 38.7 kcal/mol. The formation of M11 is predicted to be highly exoergic by 45.2 kcal/mol which further produces a long lived specie M11 that acts as a direct source for the experimentally observed product CBT. The removal of the out-of-plane H atom from M11 produces CBT in a slightly endothermic reaction of 8.0 kcal/mol. The M12 intermediate is formed by combination of C_5H_4Cl and chlorocyclopentadiene thiol radicals. M12 undergoes a three-membered ring closure step to produce the metastable tricyclic adduct, M13, in an endothermic reaction of 11.2 kcal/mol. M14 then rearranges itself via exothermic reaction (-12.4 kcal/mol) into the more stable M15, by ring isomerisation with a much lower barrier of -19.5 kcal/mol in comparison to the barrier of ring closure (M12→M13) that amounts to 14.9 kcal/mol. The bicyclic mesomer, M14, follows three-membered ring closure arrangement and forms a tricyclic radical M15. The reaction endothermicity and energy barrier for the formation of the M15 radical amount to 5.9 and 12.9 kcal/mol, respectively. The five-membered ring structure of M15 then expands and leads to the formation of M16 with a barrier of 13.3 kcal/mol in an exceedingly exothermic reaction of -20.7 kcal/mol. M16 is a precursor for the formation of CNT via self-elimination of the out-of-plane H atom.

In order to validate our results, we compared our findings with the corresponding reactions in oxygenated system. Generally the results reveal the nominal difference in the enthalpic profiles of two systems. For instance, the energy barrier for the initial ring contraction step in 4-chlorothiophenoxy radical is 15.2 kcal/mol higher than the analogous step encountered in phenoxy system (M1→M2)[10]. Furthermore, activation enthalpies for the ring closure step for CNT system along the reaction (M12→M13) are calculated to be 1.9 kcal/mol higher in reference to naphthalene system[11]. Obviously these differences of two systems can be attributed to dissimilar properties of C-O and C-S bonds linkages discussed in detail elsewhere[2]. Table 1 lists the reaction rate parameters for pathways shown in Fig. 3.

In conclusion this study presents the thermal decomposition of 4-CTP offering seven congeners of PCDT and its oxygenated analogue (PCDF), and twelve VOC species. PCDT and PCDF forms at temperature in excess of 500 °C. By constructing potential energy surfaces, we have demonstrated pathways leading to

the formation of CBT and CNT. C_5H_4Cl radical, acts as an important precursor for the formation of both species. Results concur closely with the analogous reactions of oxygenated system of the previous study.

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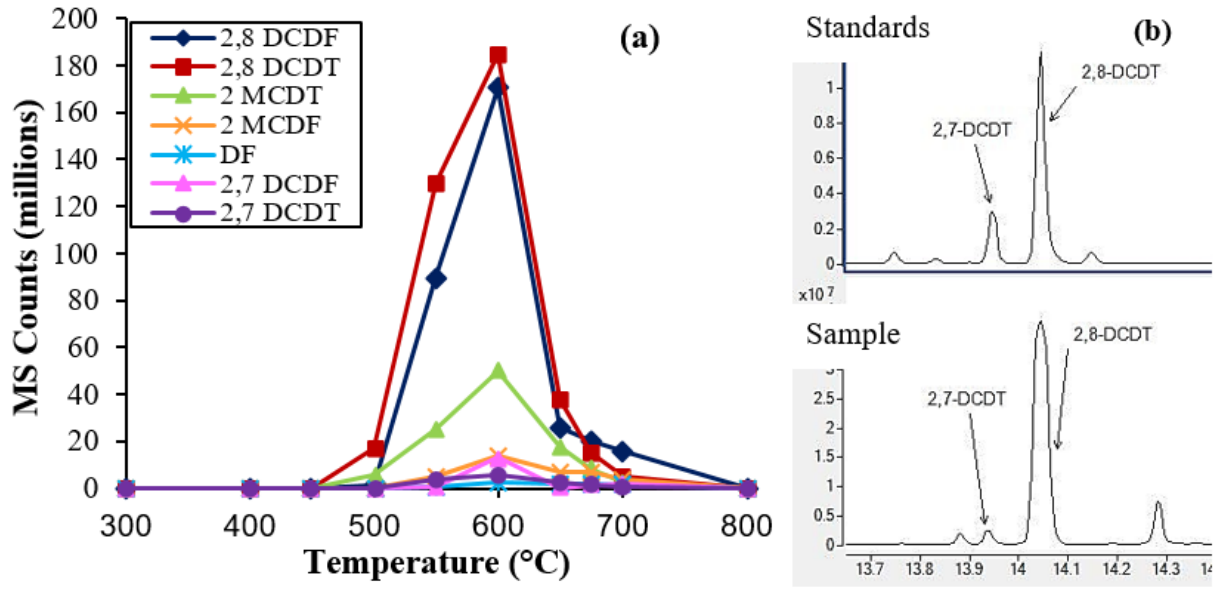

Figure 1. (a) Dioxin and its like products from gas phase oxidation of 4-CTP for a reaction time of 2 s. **(b)** identification of congeners in DCDT homologue group (counts vs time (mins))

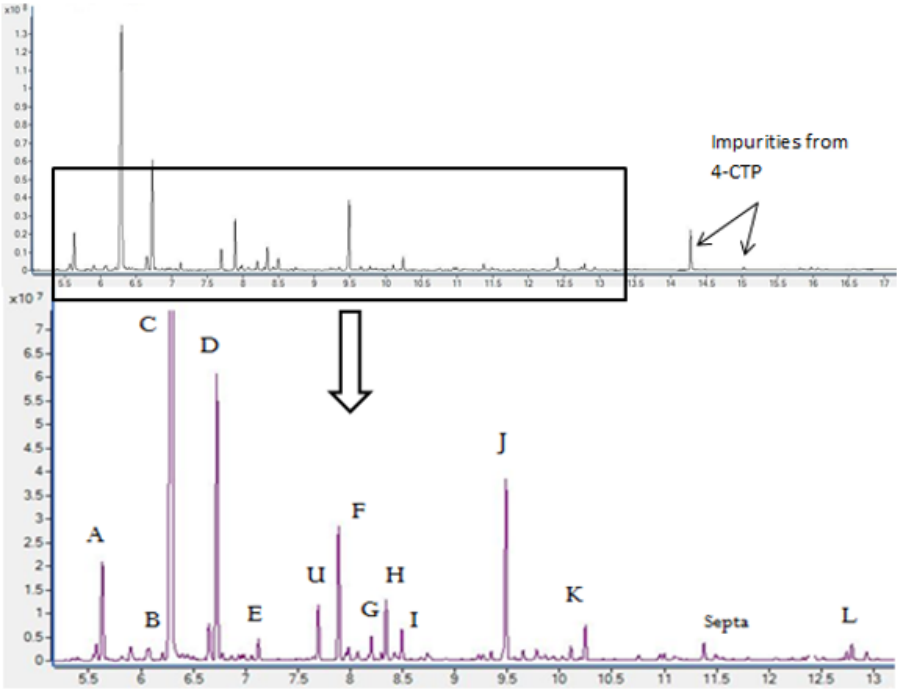

Figure 2. An example of GC trace (counts vs time) for the oxidation of 4-CTP. (A: 4-chlorobenzaldehyde; B: 2,4-dichlorophenol; C: 4-chlorophenol; D:4-chlorophenyl ester acetic acid; E: 4-chloromethyl thiobenzene; F:2-methylbenzofuran; G: 2-chloronaphthalene; H: 4-chlorobenzothiophene; I: 4-chloro-2-methylbenzofuran; J: 2,4-dichloro-2-methyl benzofuran; K: 7-chloronaphthalne thiol; L: 2,8-dichloro-diphenyl sulphide)

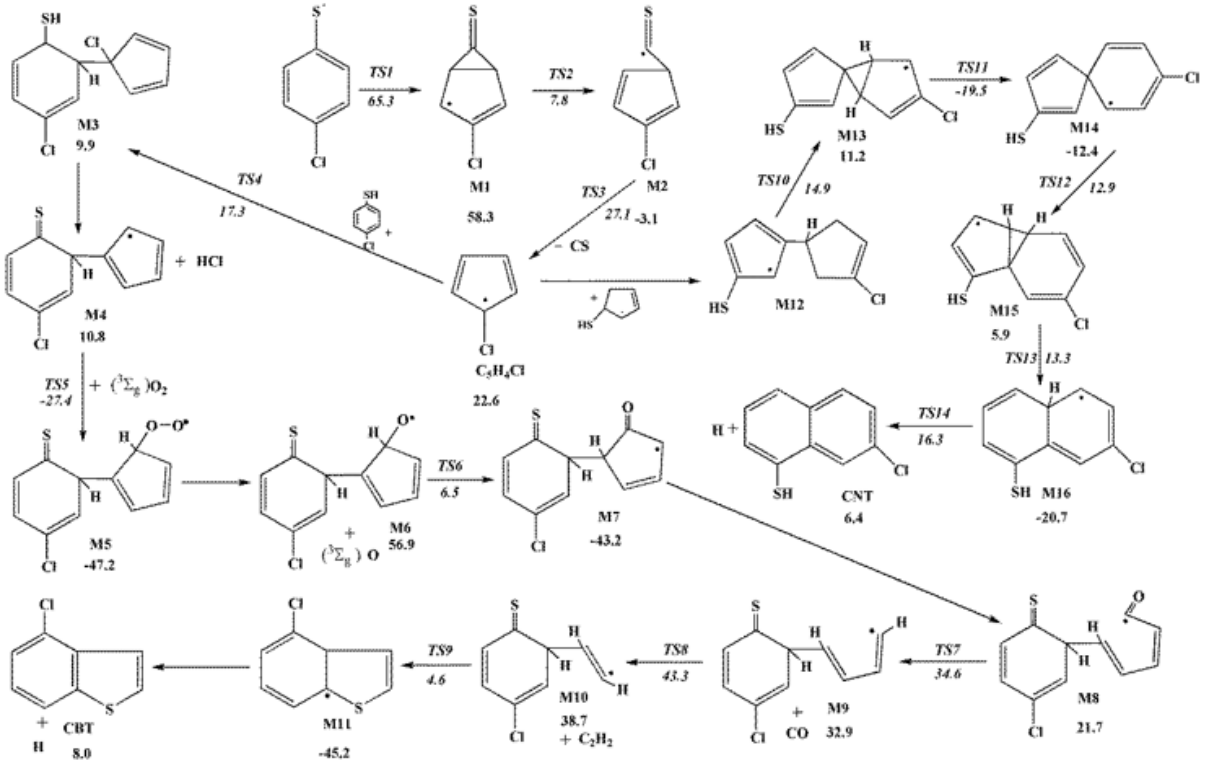

Figure 3. Pathways for the formation of C_5H_4Cl radical, CBT, CNT. Values in bold are reaction enthalpies and values in italic are activation enthalpies. All values are in kcal/mol.

Table 1. Arrhenius parameters for elementary reactions involved in the formation of CBT and CNT from 4-CTP fitted over the temperature range of 300-1200 K.

Reactions	**Forward rate parameters**		
	A **(1/s or cm^3/molecule·s)**	***n***	***E*a/R (1/K)**
CTP + C_5H_4Cl → M1	2.53×10^{-27}	3.67	8170
M4 → M5	3.13×10^{11}	0.14	25260
M6 → M7	4.90×10^{11}	0.53	17640
M7 → M8 + C_2H_2	2.91×10^{10}	1.10	21830
M11 → M12	2.87×10^{11}	0.16	7760
M13 → M14	1.53×10^{12}	0.19	3780
M14 → M15	3.46×10^{11}	0.23	17500
M15 → CNT + H	1.57×10^{12}	0.05	8470