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Formation of Persistent Organic Pollutants from 2,4,5-trichlorothiophenol Combustion: A Density Functional Theory Investigation

Tajwar Dar^a, Kalpit Shah^a, Behdad Moghtaderi^a, Alister J. Page^{a,*}

^a *Newcastle Institute for Energy and Resources, The University of Newcastle, Callaghan, NSW 2308, Australia*

* Corresponding author: alister.page@newcastle.edu.au

Abstract

Polychlorinated dibenzothiophene (PCDT) and polychlorinated thianthrene (PCTA) are sulfur analogues of dioxins such as polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F). In this work we present a detailed mechanistic and kinetic analysis of PCDT and PCTA formation from the combustion of 2,4,5-trichlorothiophenol. It is shown that the formation of these persistent organic pollutants is more favourable, both kinetically and thermodynamically, than their analogous dioxin counterparts. This is rationalized in terms of the different influences of the S-H and O-H moieties in the 2,4,5-trichlorothiophenol and 2,4,5-trichlorophenol precursors. Kinetic parameters also indicate that PCDT yield should exceed that of PCDD. Finally, we demonstrate here that the degree and pattern of chlorination on the 2,4,5-trichlorothiophenol precursor leads to subtle thermodynamic and kinetic changes to the PCDT/PCTA formation mechanisms.

Keywords: Dioxin; chlorinated; thiophene; thianthrene; persistent organic pollutant; combustion

1. Introduction

Polychlorinated dibenzothiophene (PCDT) and polychlorinated thianthrene (PCTA) are sulfur analogues of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F), i.e. dioxins [1]. Due to their structural similarity, PCDT and PCTA exhibit ecotoxicological and toxicological properties similar to those displayed by their dioxin analogues [2, 3]. However, the replacement of oxygen with sulfur increases carcinogenic and mutagenic effects in PCDT and PCTA. For instance, Nakai *et al.* [4] reported the toxic equivalency factor of PCDT to be 0.1, with respect to 2,3,7,8-tetrachlorodibenzodioxin, indicating its potential to cause dioxin-like endocrine-disruption. The cytotoxicity and dioxin-like activities of PCDT congeners in mice has also been confirmed [5]. Due to their stability and resistance to chemical/metabolic degradation, PCDT and PCTA are known to bioaccumulate and have been detected in environmental contexts as diverse as sediments [6-8] waste incineration by-products [9], oil spills [10], pulp mill effluent [11] and marine organisms [12].

It is therefore critical to have a detailed mechanistic understanding of how these persistent organic pollutants form. It is well established that the combustion of coal and biomass, municipal waste incineration, metallurgical processes and automobile exhaust are the principal sources of PCDT and PCTA in the environment. There is close correlation between the concentrations of PCDT and PCTA, and their dioxin analogues, indicating that similar chemical mechanisms dictate their formation during combustion [13]. Furthermore, since chlorinated hydrocarbons (1,3-dichloropropene [14-16] and particularly chlorophenols [17]) are known to be key precursors of PCDD and PCDF during combustion, it is likely that chlorothiophenol is a precursor for the formation of the PCDT and PCTA analogues. A previous report has demonstrated that the presence of sulfur in the precursor moiety, as opposed to oxygen, lowers enthalpic barriers in this respect [18]. However little is known

regarding the effect that increasing chlorine substitution will have on the PCDT and PCTA ratio. A recent study [19] reports the formation of PCTA from 2,4,6-trichlorothiophenol. Two pathways for radical/radical interactions were investigated for two different PCTA congeners, while PCDT was not considered. It is unlikely that condensation of 2,4,6-trichlorothiophenol would yield both PCDT and PCTA; PCTA formation requires condensation of two chlorothiophenol moieties, each with at least one *ortho*-chlorine, while PCDT formation requires two chlorothiophenols with at least one available *ortho*-hydrogen [20, 21]. On the other hand, the 2,4,5-trichlorothiophenol precursor possesses both *ortho* hydrogen and *ortho* chlorine, and so may potentially form both PCDT and PCTA *via* related chemical pathways.

Herein we investigate this possibility by reporting a theoretical investigation into the formation of PCDT and PCTA *via* the thermal decomposition of 2,4,5-trichlorothiophenol. We show that oxidative thermal decomposition of 2,4,5-trichlorothiophenol yields three different congeners of PCDT, including 2,3,7,8- tetrachlorothianthrene (TeCTA), 1,2,4,7,8- pentachlorothianthrene (PeCTA) and 1,2,4,6,7,9- hexachlorothianthrene (HxCTA). The formation of PCDT and PCTA involves smaller barriers compared to the analogous oxygenated PCDD/F species, which is ascribed to the relative strengths of the S-H and O-H bonds. Calculated Arrhenius parameters show that PCTA and PCDT formation is kinetically limited by the unimolecular elimination of H, and the cyclisation of the keto-enol moiety, respectively.

2. Computational Methods

Reactive pathways of PCTA/PCDT formation were calculated using density functional theory, *via* the hybrid B3LYP [22, 23] exchange-correlation functional, in conjunction with a 6-311G+(d,p) basis set. The QST3 algorithm was employed for the location of all transition

state (TS) structures. All TS structures were verified *via* harmonic vibrational frequency analysis. Intrinsic reaction coordinate pathways were constructed to ensure each corresponded to the correct reactant/product structures (i.e. by optimising IRC endpoint geometries to obtain reactive intermediate structures). Reaction/activation enthalpies ($\Delta_{\text{rxn}}H / \Delta H^\ddagger$) for each step were calculated using the harmonic oscillator approximation at 298 K. Kinetic analyses were then performed on the basis of conventional transition state theory. The accuracy of the B3LYP functional in the study of high temperature combustion reactions has also been widely demonstrated [24-26]. This is also the case regarding PCDD/F heats of formation [27]. The Gaussian09 [28] program was used to perform all structural and energy calculations. Kinetic parameters were calculated in the high pressure limit using ChemRate [29].

3. Results and Discussion

3.1. Radical Initiation of 2,4,5-Trichlorothiophenol Precursor

2,4,5-trichlorothiophenol exists as *syn* and *anti* conformers (see Supporting Information, Figure S1). Our calculations predict that *syn* is marginally lower in energy (0.2 kcal/mol) than *anti*. This is attributed to stabilisation from the Cl-H halide bond between the thiol group and the *ortho* Cl atom, which is present for the *syn* isomer, but absent in the *anti* isomer. The conformational enthalpic barrier is 1.8 kcal/mol using B3LYP. *syn-anti* interconversion is therefore anticipated to be frequent at typical combustion temperatures. However *syn* is anticipated to be the dominant isomer (according to the Boltzmann factor, $e^{(\Delta H_{\text{syn}} - \Delta H_{\text{anti}})/kT}$), constituting > 90% at temperatures above 1,000 K. On this basis, the remainder of our discussion pertains to reactive pathways originating with *syn*-2,4,5-trichlorothiophenol.

Homogeneous gas phase formation of PCDT and PCTA from 2,4,5-trichlorothiophenol potentially involves radical/radical, radical/molecule and molecule/molecule coupling reaction pathways. A previous investigation [30] demonstrated that, of these pathways, radical/radical dimerization is most predominant for the formation of PCDT and PCTA. This pathway is initiated by the loss of thiol hydrogen from 2,4,5-trichlorothiophenol, forming the 2,4,5-trichlorothiophenoxy radical. This can occur *via* both unimolecular and bimolecular processes, as shown in Table 1. B3LYP predicts the unimolecular scission of the S-H bond in 2,4,5-trichlorothiophenol to be a barrierless, yet highly endothermic process ($\Delta_{\text{rxn}}H = 77.5$ kcal/mol). Abstraction of thiol hydrogen by ($^3\Sigma_g$)O₂ yields the largest enthalpic barrier of those reactions considered ($\Delta H^\ddagger = 10.7$ kcal/mol), and results in the exothermic formation of HO₂ and 2,4,5-trichlorothiophenoxy radicals. Abstraction of thiol hydrogen by both H and (^3P)O radicals is barrierless and exothermic ($\Delta_{\text{rxn}}H = -27.1, -24.9$ kcal/mol, respectively), whereas abstraction by Cl incurs a barrier of 3.5 kcal/mol, according to B3LYP.

Table 1. $\Delta H^\ddagger$ and $\Delta_{\text{rxn}}H$ for formation of 2,4,5 trichlorothiophenol radical (TCTP•) from 2,4,5 trichlorothiophenol (TCTP)

	$\Delta H^\ddagger$ (kcal/mol)	$\Delta_{\text{rxn}}H$ (kcal/mol)
2,4,5 TCTP $\rightarrow$ 2,4,5 TCTP• + H	-	77.5
2,4,5 TCTP + H $\rightarrow$ 2,4,5 TCTP• + H ₂	-	-27.1
2,4,5 TCTP + OH $\rightarrow$ 2,4,5 TCTP• + H ₂ O	1.5	-37.4
2,4,5 TCTP + (^3P)O $\rightarrow$ 2,4,5 TCTP• + OH	-	-24.9
2,4,5 TCTP + ($^3\Sigma_g$)O ₂ $\rightarrow$ 2,4,5 TCTP• + HO ₂	10.7	-9.3
2,4,5 TCTP + Cl $\rightarrow$ 2,4,5 TCTP• + HCl	3.5	-22.6

These results show that, generally, abstraction of S-H hydrogen from 2,4,5-trichlorothiophenol is more enthalpically favourable compared to the abstraction of O-H

hydrogen from trichlorophenol (i.e. the non-sulfurous analogue). For instance, for trichlorophenol, H abstraction with H (i.e. forming trichlorophenoxy radical and molecular H₂) amounts to a reaction barrier of 13.9 kcal/mol [31] using MPWB1K/6-31+G(d,p), while the analogous reaction is found to be barrierless for trichlorothiophenol. Similarly, H abstraction from trichlorothiophenol by OH is 10 kcal/mol more exothermic compared to the same abstraction reaction in the oxygenated system. This is a direct consequence of the difference in O/S-H bond strengths; the S-H bond (77 kcal/mol) [32] in thiophenol is weaker than the O-H (87 kcal/mol) [33, 34] bond in phenol, based on DFT (BB1K exchange correlation functional [35]) and CBS-QB3 [36, 37] levels of theory respectively. Decomposition of trichlorothiophenol will therefore be initiated at lower thermal temperatures by comparison, making trichlorothiophenol a more effective reaction precursor. Previous studies have also shown that thiophenoxy sulfur atoms exhibit less radical character compared to phenoxy oxygen atoms, on account of dissimilar bond shortening (C-S/O) during radical formation. Furthermore dimerization of chlorophenols is expected to be more favourable compared to the corresponding reaction of chlorothiophenol due to the higher nucleophilicity of the phenoxy radical.

3.2. PCTA Formation Mechanism and Kinetics

Figure 1 presents a detailed mechanism for the formation of three congeners of thianthrenes (2,3,7,8-TeCTA, 1,2,4,7,8-PeCTA and 1,2,4,6,7,9-HxCTA). Geometries for all the TS structures in Figure 1 are shown in Figure 2.

Figure 1. Formation of 2,3,7,8-TeCTA and 1,2,4,7,8-PeCTA and 1,2,4,6,7,9-HxCTA from dimerization of 2,4,5-trichlorothiophenol radical. Values in bold are reaction enthalpies and values in italic are activation enthalpies in reference to the reactants in each reaction. All values are in kcal/mol at 298.15 K.

The combination of two trichlorothiophenoxy radicals produces two mesomers; M1 *via* TS1 and M4 *via* a barrierless reaction. Formation of M1 requires activation enthalpies of 2.4 kcal/mol. The formation of M1 and M4 are both exoergic, by 0.8 and 5.8 kcal/mol respectively. M1 can then undergo bimolecular reaction with ambient H/OH/Cl radicals. Abstraction of Cl atom by H, OH and Cl radicals from the C-S bridge in M1 occurs with low reaction barriers of 0.9 (TS2), 7.7 (TS3) and 3.2 kcal/mol (TS4), and are each highly exothermic. Further reaction of M2 involves ring closure, accompanied by intramolecular Cl elimination, producing 2,3,7,8-TeCTA in an endothermic reaction ($\Delta_{\text{rxn}}H = 13.4$ kcal/mol)

through a reaction barrier of 19.2 kcal/mol (TS5). Additionally, M2 mesomer can undergo cyclization to form M3. $\Delta H^\ddagger$ for this reaction is only 2.6 kcal/mol (TS6), while $\Delta_{\text{rxn}}H$ is exothermic by 9.5 kcal/mol. Hydrogen elimination from M3 *via* TS7 results in the formation of 1,2,4,7,8-PeCTA. This reaction has a high kinetic barrier ($\Delta H^\ddagger = 36.2$ kcal/mol), despite being significantly exoergic ($\Delta_{\text{rxn}}H=30.3$ kcal/mol). Condensation of the 2,4,5 trichlorothiophenoxy radical at the *ortho* position results in the M4 moiety. The elongation of the C-H bond in M4 by 1.1 Å indicates that hydrogen abstraction by radical H, OH and Cl is more likely. Each of these abstraction reactions are barrierless, and highly exothermic ($\Delta_{\text{rxn}}H = -50.8, -61.1$ and -46.3 kcal/mol, respectively). The resulting pre-dioxin intermediate M5 branches into three competing channels. The first channel involves cyclization and Cl elimination *via* TS8, producing 1,2,4,7,8-PeCTA with a modest activation enthalpy of 8.5 kcal/mol. 1,2,4,6,7,9-HxCTA is produced *via* the second channel, which consists of ring closure (M5 $\rightarrow$ M8) and subsequent hydrogen elimination (M8 $\rightarrow$ 1,2,4,6,7,9-HxCTA). Unsurprisingly, $\Delta H^\ddagger$ for the former reaction (4.0 kcal/mol, TS9) is substantially smaller than that for the latter (36.5 kcal/mol, TS10). 1,2,4,7,8-PeCTA can also be formed from M5 *via* a Smiles rearrangement (M5 $\rightarrow$ M6 $\rightarrow$ M7 $\rightarrow$ 1,2,4,7,8-PeCTA). Each step in this reaction is associated with modest enthalpic barriers, with $\Delta H^\ddagger = 8.1$ kcal/mol (TS11), 7.0 kcal/mol (TS12) and 1.9 kcal/mol (TS13), respectively.

Figure 2. Transition state structures for the reaction scheme in Figure 1. Interatomic distances are in Å.

Knowledge of experimental conditions, including reactor temperature, geometry, flow-rates etc., and concentration of radicals are necessary in order for a complete kinetic conclusion to be derived. For these reasons such an analysis lies beyond the scope of this investigation; here, we aim to overview kinetic parameters of pertinent radical initiation pathways associated with PCDT and PCTA formation. Table 2 lists calculated Arrhenius parameters for steps in the PCTA formation mechanism proposed in Figure 1, fitted using the high-pressure limit between a temperature range of 300 – 1200 K. Table 2 indicates that the cyclisation of M2 into M3 is more kinetically labile than the ring closure of M2 into 2,3,7,8-TeCTA. Thus, the formation of 1,2,4,7,8-PeCTA is kinetically preferred over the formation

of 2,3,7,8-TeCTA. However, high activation enthalpy in the latter step (36.2 kcal/mol) makes the concerted reaction of 2,3,7,8-TeCTA preferred over the formation of 1,2,4,7,8-PeCTA.

Results presented here demonstrate that the formation of PCTA from trichlorothiophenol is kinetically more favourable, compared to PCDD formation from trichlorophenol. Formation of PCTA is associated with consistently lower enthalpic barriers compared to the formation of PCDD. For instance, for the $M5 \rightarrow 1,2,4,7,8\text{-PeCTA}$ cyclization reaction exhibits, we show here that this barrier height is 8.5 kcal/mol, while that for the oxygenated system is 27.2 kcal/mol [31]. Similarly, the formation of 2,3,7,8-TeCTA has an enthalpic barrier of 13.4 kcal/mol, which is lower (yet more comparable) to that for the oxygenated analogue, 15.1 kcal/mol [31].

Table 2. Arrhenius parameters for elementary reactions involved in the formation of PCTA from 2,4,5-TCTP between 300-1200 K.

	A	n	E_a (kcal/mol)
$\text{TCTP} + \text{H} \rightarrow \text{TCTP}\cdot + \text{H}_2$	$1.51 \times 10^{-15}{}^a$	1.4	0.3
$\text{TCTP} + \text{OH} \rightarrow \text{TCTP}\cdot + \text{OH}_2$	$1.32 \times 10^{-19}{}^a$	2.8	1.2
$\text{TCTP} + \text{Cl} \rightarrow \text{TCTP}\cdot + \text{HCl}$	$2.19 \times 10^{-16}{}^a$	1.4	7.8
$\text{TCTP} + \text{O}_2 \rightarrow \text{TCTP}\cdot + \text{HO}_2$	$1.36 \times 10^{-21}{}^a$	2.6	10.9
$\text{M1} + \text{H} \rightarrow \text{M2} + \text{HCl}$	$5.43 \times 10^{-15}{}^a$	1.5	0.4
$\text{M1} + \text{OH} \rightarrow \text{M2} + \text{HOCl}$	$1.11 \times 10^{-19}{}^a$	2.4	7.0
$\text{M1} + \text{Cl} \rightarrow \text{M2} + \text{Cl}_2$	$2.82 \times 10^{-16}{}^a$	1.8	3.0
$\text{M2} \rightarrow 2,3,7,8\text{-TeCTA} + \text{Cl}$	$2.83 \times 10^9{}^a$	0.9	19.4
$\text{M2} \rightarrow \text{M3}$	$1.89 \times 10^{11}{}^b$	0.2	0.5
$\text{M3} \rightarrow 1,2,4,7,8\text{-PeCTA} + \text{H}$	$1.95 \times 10^9{}^a$	1.3	30.1
$\text{M4} + \text{H} \rightarrow \text{M5} + \text{H}_2$	$2.89 \times 10^{-16}{}^a$	1.4	42.1
$\text{M4} + \text{Cl} \rightarrow \text{M5} + \text{HCl}$	$3.10 \times 10^{-19}{}^a$	2.3	15.3
$\text{M5} \rightarrow 1,2,4,7,8\text{-PeCTA} + \text{Cl}$	$1.12 \times 10^{11}{}^b$	0.3	8.9
$\text{M5} \rightarrow \text{M6}$	$6.18 \times 10^{10}{}^b$	0.4	0.4
$\text{M6} \rightarrow \text{M7}$	$4.60 \times 10^{12}{}^b$	0	8.1
$\text{M7} \rightarrow 1,2,4,7,8\text{-PeCTA} + \text{Cl}$	$1.57 \times 10^{12}{}^b$	0.05	16.8
$\text{M5} \rightarrow \text{M8}$	$8.41 \times 10^{10}{}^b$	0.2	0.5
$\text{M8} \rightarrow 1,2,4,6,7,9\text{-HxCTA} + \text{H}$	$2.60 \times 10^{11}{}^a$	1.5	30.4

^a $\text{cm}^3 \text{ molecule}^{-1} \text{ s}$

^b s^{-1}

3.3. PCDT Formation Mechanism and Kinetics

We turn now to a discussion of PCDT formation from 2,4,5-trichlorothiophenol. Figure 3 depicts formation of 1,2,4,6,8,9-hexachlorodibenzothiophene (1,2,4,6,8,9-HxCDT). Corresponding TS structures are provided in Figure 4.

The open shell pathway ($M9 \rightarrow M10 \rightarrow M11 \rightarrow M12 \rightarrow 1,2,4,6,8,9\text{-HxCDT}$) shown in Figure 3 involves five elementary steps. Initially, dimerization of the trichlorothiophenol radical precursor occurs at the *ortho* positions, forming M9 *via* TS14 which has an enthalpic barrier of 27.7 kcal/mol and is endoergic by 17.3 kcal/mol. A single H abstraction from the newly-formed C-C bond then takes place ($M9 \rightarrow M10$) by radical H and OH. These reactions have zero activation enthalpies. Tautomerisation then leads to the formation of a thiol moiety ($M10 \rightarrow M11$). $\Delta H^\ddagger$ for this migration is almost negligible, 2.9 kcal/mol. Electrocyclic ring closure ($M11 \rightarrow M12$) and elimination of the thiol group finally leads to 1,2,4,6,8,9-HxCDT. The former of these steps is associated with a significant activation enthalpy of 18.9 kcal/mol (TS16), whereas the latter has a small barrier of only 1.7 kcal/mol (TS17).

Figure 3. Formation of 1,2,4,6,8,9-HxCDT from dimerization of 2,4,5-trichlorothiophenol radical. Values in bold are reaction enthalpies and values in italic are activation enthalpies in reference to the reactants in each reaction. All values are in kcal/mol at 298.15 K.

The alternative pathway to 1,2,4,6,8,9-HxCdT shown in Figure 3 is a closed shell. In this case, the formation of M10 is replaced by the formation of M13 from the M9 dimer. Here, M13 is the result of tautomerisation across the *ortho/ortho* coupled C-C bond in M9, forming two thiol groups. Unsurprisingly, this migration has a relatively small barrier TS18 ($\Delta H^\ddagger = 9.5$ kcal/mol) and is highly exoergic ($\Delta_{\text{rxn}}H = -51.6$ kcal/mol). M11 can then be formed *via* favourable H abstraction by ambient radical species such as H/Cl/OH (only H is considered in Figure 3, for which $\Delta H^\ddagger = 0.2$ (TS19) and $\Delta_{\text{rxn}}H = -25.8$). 1,2,4,6,8,9-HxCdT can then be formed *via* M12 as described above.

Figure 4. Transition structures for the intermediates and products involved in the formation of Figure 3 and 5. Interatomic distances are in Å.

An alternative pathway to PCDT formation from trichlorothiophenol can occur *via ortho/ortho* coupling at Cl and H sites, as depicted in Figure 5. This coupling would result in the formation of 1,2,4,7,8-PeCDT *via* a similar reactive pathway to that discussed in Figure 3. Here, however, Cl abstraction from the newly formed C-C bond in M14 is required before

tautomerisation and electrocyclic ring closure. We consider two possibilities, Cl abstraction by H and OH radicals, forming HCl and HOCl, respectively. Both reactions are highly exothermic ($\Delta_{\text{rxn}}H = -95.8$ and -42.7 kcal/mol, respectively). The higher exothermicity for HCl formation follows from the relative strengths of the H-Cl and H-O bonds. HOCl formation is bound by a low barrier ($\Delta H^\ddagger = 0.3$ kcal/mol, TS20), while HCl formation has barrier of 2.9 kcal/mol (TS21). The subsequent tautomerisation of M15 $\rightarrow$ M16 exhibits an enthalpic barrier slightly higher to that observed for the M10 $\rightarrow$ M11 tautomerisation reaction shown in Figure 3 ($\Delta H^\ddagger = 15.3$ kcal/mol versus $\Delta H^\ddagger = 2.9$ kcal/mol, respectively). Similarly, M15 $\rightarrow$ M16 is significantly less exothermic compared to M10 $\rightarrow$ M11 ($\Delta_{\text{rxn}}H = -10.8$ kcal/mol versus $\Delta_{\text{rxn}}H = -25.4$ kcal/mol). This indicates that decreasing the extent of Cl substitution in the M9 dimer impedes PCDT formation, both kinetically and thermodynamically. Conversely, the M16 $\rightarrow$ M17 ring closure exhibits an enthalpic barrier lower than that for M11 $\rightarrow$ M12 ring closure ($\Delta H^\ddagger = 16.5$ kcal/mol versus 18.9 kcal/mol, respectively). The extent and position of chlorine substitution in PCDT and PCTA therefore influences subtly the nature of these reactive pathways. We note also that the reactive pathways for PCDT formation require lower activation barriers than those for PCDF, which is attributed to the differences induced by the presence of sulfur. For instance, tautomerisation of M9 into M13 requires overcoming the reaction barrier of 9.5 kcal/mol, ~ 10 kcal/mol lower than the corresponding oxygenated system [31].

Figure 5. Formation of 1,2,4,7,8-PeCDT from dimerization of 2,4,5-trichlorothiophenol radical. Values in bold are reaction enthalpies and values in italic are activation enthalpies in reference to the reactants in each reaction. All values are in kcal/mol at 298.15 K.

Table 3. Arrhenius parameters for elementary reactions involved in the formation of PCTA from 2,4,5-TCTP fitted over the temperature range of 300-1200 K.

	<i>A</i>	<i>n</i>	<i>E_a</i> (kcal/mol)
M9 + OH → M10 + H ₂ O	3.17×10^{-22} ^a	2.6	19.2
M9 + Cl → M10 + HCl	2.86×10^{-19} ^a	2.1	8.1
M10 → M11	4.40×10^{10} ^b	0.7	3.8
M11 → M12	1.76×10^{11} ^b	0.2	19.7
M12 → 1,2,4,6,8,9-HxCdT + SH	4.43×10^{12} ^b	0.2	0.5
M9 → M13	1.39×10^{10} ^b	1.2	13.0
M13 + H → M11 + H ₂	1.24×10^{-15} ^a	1.5	0.5
M14 + H → M15 + HCl	3.45×10^{-15} ^a	1.5	0.6
M14 + OH → M15 + HOCl	5.88×10^{-20} ^a	2.3	1.2
M14 + Cl → M15 + Cl ₂	3.85×10^{-16} ^a	1.6	20.9
M15 → M16	5.08×10^{11} ^b	0.5	5.7
M16 → M17	9.44×10^{10} ^b	0	5.4
M17 → 1,2,4,7,8-PeCDT + SH	6.92×10^{12} ^b	0.05	0.6

^a cm³ molecule⁻¹ s

^b s⁻¹

To the best of our knowledge there are no experimental kinetic parameters available for PCDT formation from 2,4,5-trichlorothiophenol. In order to validate the kinetic parameters calculated here (Table 3), we compare them with literature values pertaining to the formation of dioxins from 2,4,5-trichlorothiophenol. Our calculated rate constants are generally higher

than the corresponding values reported by Qu *et al.* [31] by one order of magnitude. For example, our calculated value of A for ring closure ($M11 \rightarrow M12$) is $1.76 \times 10^{11} \text{ s}^{-1}$ at 800 K, whereas that pertaining to PCDD/F formation is $4.18 \times 10^{10} \text{ s}^{-1}$. We note however that the Arrhenius parameters for the H shift reaction in the present work ($A = 4.40 \times 10^{10} \text{ s}^{-1}$) are in good agreement with those for the analogous oxygenated reaction ($A = 3.37 \times 10^{10} \text{ s}^{-1}$).

A comparison of the kinetic parameters presented in Tables 2 and 3 facilitates a prediction of the relative PCDT/PCTA yields from the 2,4,5-trichlorophenol precursor. We anticipate PCDT to be the dominant product species, based on this comparison. For example, for the formation of 1,2,4,7,8-PeCTA *via* reaction $M5 \rightarrow 1,2,4,7,8\text{-PeCTA} + \text{Cl}$, $A = 1.12 \times 10^{11} \text{ s}^{-1}$ (Table 2). However, the formation of PeCDT from M17 corresponds to $A = 6.92 \times 10^{12} \text{ s}^{-1}$ (Table 3). Similarly, the formation of 1,2,4,6,8,9-HxCdT and SH from M12 corresponds to $A = 4.43 \times 10^{12} \text{ s}^{-1}$ (Table 3) whereas the analogous step for the formation of 1,2,4,6,7,9-HxCtA (from M11) corresponds to $A = 2.60 \times 10^{11} \text{ s}^{-1}$ (Table 2). This trend is consistent with previously reported experimental results showing that, during oxidative decomposition of trichlorophenol, PCDF yield (analogous to PCDT) exceeds that of PCDD (analogous to PCTA) [38].

4. Conclusions

We have presented an investigation of the oxidative decomposition of 2,4,5-trichlorophenol, forming PCDT and PCTA. Density functional theory calculations establish five distinct reaction channels for the formation of three isomers of PCTA, 2,3,7,8-TeCTA, 1,2,4,7,8-PeCTA and 1,2,4,6,7,9-HxCtA. The formation of 2,3,7,8-TeCTA and 1,2,4,7,8-PeCTA *via* routes 1, 3 and 5 are thermodynamically preferable over pathways 2 and 4, due to lower activation enthalpies. The formation of two isomers of PCDT (1,2,4,6,8,9-HxCdT and 1,2,4,7,8-PeCDT) can also take place *via* five elementary steps. For both PCDT

and PCTA, reaction energy profiles are generally lower, compared to the same reactive pathways in the oxygenated analogue species. This is rationalized in terms of the different influences of the S-H and O-H moieties in 2,4,5-trichlorothiophenol and 2,4,5-trichlorophenol respectively. Calculated kinetic parameters for key reaction steps demonstrate that (1) the formation of PCDT and PCTA are generally more kinetically favourable, compared to the PCDD and PCDF analogues, and (2) PCDT formation is more favourable than PCTA from 2,4,5-trichlorothiophenol combustion. This work has also revealed that the degree and pattern of chlorination on the trichlorothiophenol precursor leads to subtle effects regarding the PCDT and PCTA formation mechanisms.

Supporting Information

Cartesian coordinates for all structures and all IRC pathways are provided in supporting information.

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