THEORETICAL STUDY IN THE DIMERISATION OF 2-CHLOROTHIOPHENOL/2-CHLOROTHIOPHENOXY: PRECURSORS TO PCDT/TA

Dar T*, Altarawneh M†, Dlugogorski B

Priority Research Centre for Energy, Faculty of Engineering & Built Environment
The University of Newcastle, Callaghan NSW 2308, Australia

† Corresponding author: Phone: (+61) 2 4985-4286,
Email: Mohammednoor.Altarawneh@newcastle.edu.au
Also at Chemical Engineering Department, Al-Hussein Bin Talal University, Ma'an, Jordan

1. Introduction

Despite wide use of chlorinated thiophenols as intermediates in organic synthesis, their role as persistent organic pollutant has not yet been fully addressed. Chlorothiophenols have found widespread applications in manufacturing of pharmaceutiacal[1], dyes, insecticides, printing inks, pesticides and polyvinyl chloride (PVC) [2, 3]. Species formed from chlorinated thiophenols are toxic and hazardous to health, with their toxicity increasing with the degree of chlorination[4]. For instance, pentachlorothiophenol, an additive in vulcanisation process of rubber in tyre industry, represents an important precursor for the formation of polychlorinated dibenzothiophenes (PCDT) and polychlorinated thianthrenes (PCTA)[5], with their structures illustrated in Fig. 1. Consensus of opinion in the literature indicates that chlorothiophenols act as precursors for the formation of PCDT/TA[6-8]. Benz et al.[5] detected and identified sulfur analogues of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F, dioxins) during manufacturing of chlorothiophenol. As PCDT/TA constitute sulfur equivalents of PCDD/F, there are 135 isomers of PCDT and 75 isomers of PCTA. From a toxicological point of view, PCDT/TA have been identified to cause endocrine disruption[9]. But, in general, these compounds are less toxic than PCDD/F with TEF of 2378-TeCTA and 2378-TeCDT as 0.01 and 0.001 respectively[10].

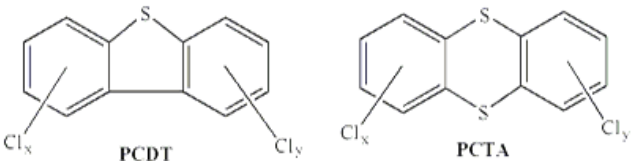

Figure 1: Structure of polychlorinated thianthrene (PCTA) and polychlorinated dibenzothiophene(PCDT)

PCDT/TA appear to form in conjunction with PCDD/F[11]. This has prompted us to suggest similar operating conditions for the formation of PCDT/TA, and to pursue the elucidation of their formation based on an analogy to the mechanism of formation of PCDD/F[12]. The principal steps in formation of PCDD/F in gas phase from chlorophenols include dimerisation of precursors (chlorophenoxy radical and chlorophenol molecules), such as coupling of molecule/molecule, radical/radical or radical/molecule, as well as intermolecular cyclisation of preformed intermediates to produce PCDD/F, and related chlorination and dechlorination reactions.

The purpose of this study is therefore to develop initial pathways for the gas phase formation of PCDT/TA and evaluate the relevant thermochemical parameters, in particular, activation energies and reaction enthalpies. In addition, the contribution compares the steps in the formation of PCDT/TA and PCDD/F to pinpoint the effect of the SH functional group.

2. Methods

Gaussian suite[13] of programs was used to perform computations at the B3LYP/6-311+G(d,p)[14] level of theory. Transition structures were linked to their reactants and products via calculations of intrinsic reaction coordinate (IRC).

3. Results and discussion

In a previous study, we have evaluated atomic polar tensor charges to confirm a higher charge density on oxygen atom of 2-chlorophenol (CP) in comparison to sulfur of 2-chlorothiophenol (CTP). The difference amounted to -0.5. PCDT/TA arise at lower temperatures than dioxins as the bond dissociation enthalpy of CP corresponds to 89 kcal mol^{-1} while that of CTP equals 77 kcal mol^{-1}, signifying a stronger O−H bond in CP than S−H bond in CTP [15].

A thiophenoxy radical forms in the decomposition of a thiophenol molecule, either by unimolecular elimination or through bimolecular reactions with the H/O radical pool. In analogy to the mechanism of formation of PCDD/F, major distinction in production of PCDT/TA stems from different precursors and coupling sequences. Firstly, formation of PCDT proceeds through self-condensation of thiophenoxy radicals while PCTA are produced by condensation reactions involving molecule/molecule, molecule/radical and radical/radical. Moreover, formation of PCDT requires two CTP molecules each with one available *ortho* hydrogen while PCTA requires at least 2 molecules of CTP, each with at least one *ortho* chlorine.

Radical/radical type coupling occurs at unchlorinated *ortho* carbon sites to produce a diketo tautomer of biphenyl dithiol. In formation of PCDT, this intermediate undergoes a keto → enol tautomerisation to form a biphenyl dithiol which subsequently eliminated HS to yield PCDT. In formation of PCTA, a carbon centred radical mesomer combines with a sulfur centred radical mesomer to form a keto ether. Following the loss of hydrogen to form thiophenoxyl diphenyl ether, mono chlorinated thianthrene (MCTA) arises through Cl· displacement or elimination of HCl.

In our discussion, we follow reaction schemes and species nomenclature adopted by Altarawneh et al.[16] in their mechanism of the formation of PCDD/F from coupling of 2-chlorophenol/2-chlorophenoxy. Self-reaction of thiophenoxy radicals through thiophenolic sulfur and the three delocalised carbon atoms afford eight isomers D1-D8 (Fig. 2). D1 and D5 result from coupling of two 2-chlorothiophenoxy radicals at *o-o* and *p-p* positions, respectively. D4 and D7 evolve from combination of thiophenolic sulfur with *para* carbons. D2 and D3, as well as D6 and D8 intermediate are sourced from *o-o* and *o-p* coupling respectively. Major precursors of PCDT are *o-o* coupled sulfur centred D1, D2 and D3. Formation of intermediate D7, i.e. direct pre-structure of PCTA, is associated with the highest exothermicity in the self-condensation of two 2-chlorothiophenoxy radicals.

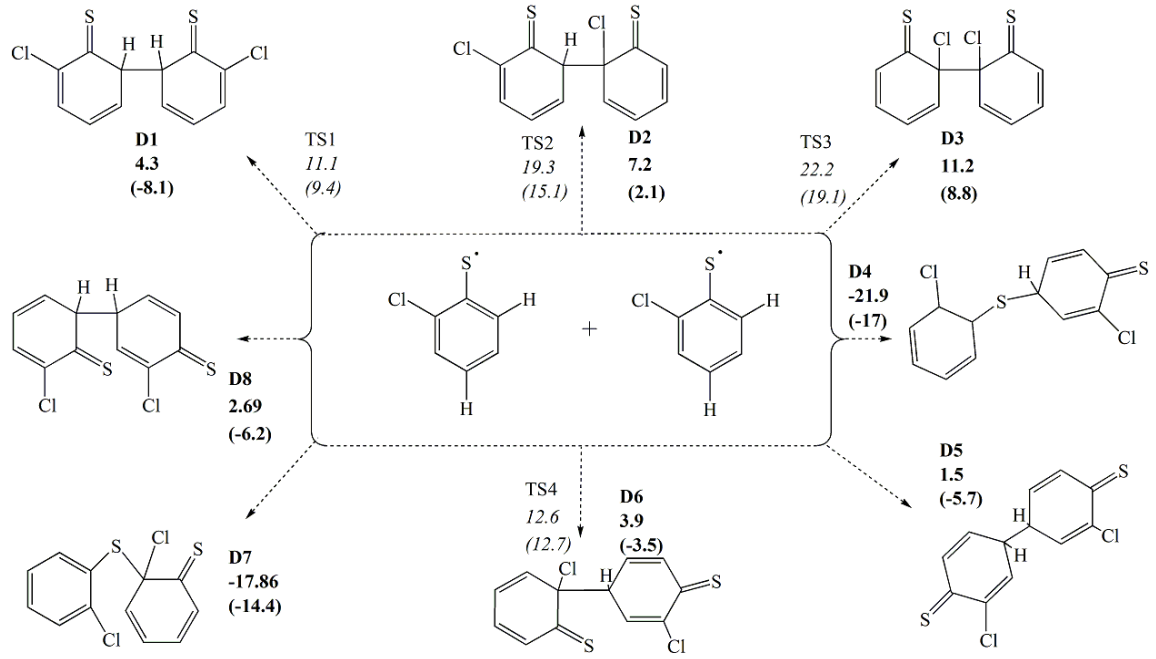

Figure 2: Stable structures from the dimerisation of two 2-chlorothiophenoxy radicals. Values in bold are reaction enthalpies and values in italic are activation enthalpies. All values are in kcal/mol. Values within the brackets are the corresponding values for self-condensation of two 2-chlorothiophenoxy radicals.

Likewise, the formation of the D1 intermediate, i.e. a direct pre-structure of PCDT, corresponds to exothermicity of 4.3 kcal/mol on the hyper energy surface. The dimerisation of 2-chlorophenoxy radicals to produce D4 (phenolic sulfur with *para* carbon coupling) represents the most exothermic reaction both for CTP and CP systems. The formation of D4 is barrierless in the case of CTP but it requires a trivial activation energy of 1.2 kcal mol^{-1} in the case of CP. The synthesis reaction of D7 from its corresponding radicals constitutes the second most exothermic process with ΔH_r of -17.86 and -14.4 kcal, from CTP and CP, respectively. The reaction is barrierless both for CTP and CP. Contrary to this, pairing of *o-o* carbon (D3) represent the most endothermic channel with the highest values of reaction and activation energies among all the structures.

Figs. 3 and 4 depict Pre PCTA structures resulting from molecule/molecule and molecule/radical coupling, respectively. Enthalpies of reaction ΔH_r and activation enthalpies $\Delta H_r^{\#}$ at 298.15 K are calculated for the formation of the three Pre PCTA structures, Pre D1, Pre D2 and Pre D3, although the channel to Pre D2 display too high activation energy for the formation of Pre D2 to be feasible. In brackets, the figures include the corresponding values from the condensation of CP molecules[16].

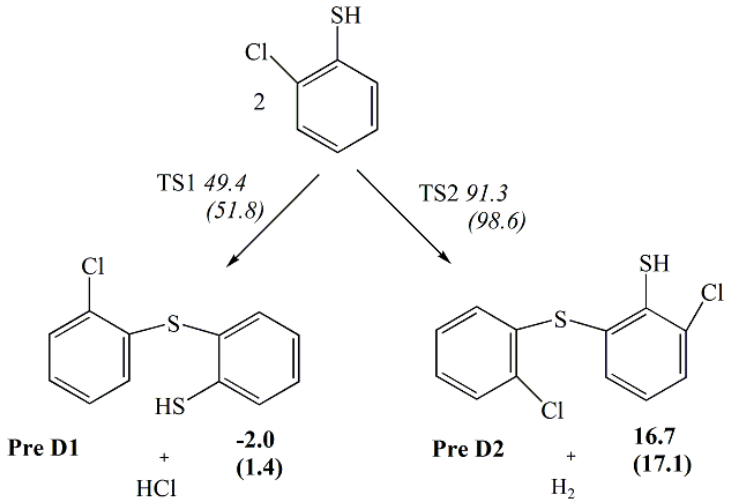

Figure 3: Self condensation of 2-CTP to Pre PCTA. Values in bold are reaction enthalpies and values in italic are activation enthalpies. All values are in kcal/mol. Values within the brackets are the analogous values for the self-coupling of two 2-chlorophenol molecules.

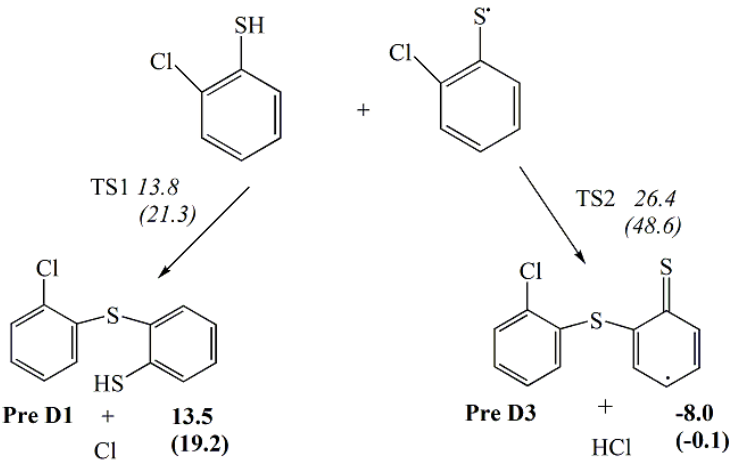

Figure 4: Pathways to pre PCTA from combustion of 2-CTP and 2-chlorothiophenoxy. Values in bold are reaction enthalpies and values in italic are activation enthalpies. All values are in kcal/mol. Values within the brackets are the analogous values for reaction of CTP with 2-chlorothiophenoxy.

As shown in Fig. 3, coupling of two CTP molecules leads to the formation of 2-(2-chlorothiophenoxy) thiophenol (Pre D1) and 2-chloro-6-(2 chlorothiophenoxy) thiophenol (Pre D2) with elimination of HCl and H_2, respectively. The production of Pre D1 is more favourable than Pre D2 based on an enthalpic reaction difference of 18.6 kcal mol^{-1}. Pre D2 structure requires an activation enthalpy as much as twice the corresponding value of Pre D1. These results agree with those for a reaction involving two 2-CP molecules.

Fig. 4 illustrates pathways for the formation of Pre D1 and Pre D3 (2-(2-chlorothiophenoxy)cyclohexane-2,5-dithioenone) from the combination of a molecule of 2-CTP and a 2-chlorothiophenoxy radical. This radical/molecule coupling produces more exothermic reaction product, Pre D3, requiring a significantly lower activation enthalpy in comparison to synthesis from CP. Formation of Pre D3 from coupling of

molecule/radical, shown in Fig. 4, is expected to be of minor importance in view of the difference in activation enthalpies associated with TS1 and TS2, as indicated in Fig. 4.

Enthalpies of formation for all plausible products are listed in Table 1. These enthalpies are based on $\Delta_f H^o_{298}$ for CTP (19.9 kcal mol^{-1})[15], chlorothiophenoxy radical (56.3 kcal mol^{-1})[15], the experimental enthalpies of formation for HCl and Cl, and the enthalpy of reactions given in Figs. 2-4.

Table 1: Standard Enthalpy of formation of CTP isomers from its molecule and radical

Species	**Enthalpy of Formation (kcal mol^{-1})**	**Species**	**Enthalpy of Formation (kcal mol^{-1})**
Figure 1			
D1	116.8	**Figure 3**	
D2	119.8	Pre D1	37.8
D3	123.8	Pre D2	56.5
D4	90.6		
D5	114.1	**Figure 4**	
D6	116.5	Pre D1	89.7
D7	94.7	Pre D3	68.2
D8	115.3		

The thermochemical data calculated for radical/molecule dimerisation of CTP concur closely with the similar results for CP of the previous study. Coupling of 2-chlorothiophenoxy radicals identifies D1 as the most favourable pre structure for the formation of PCDT, but PCTA would dominate the products on account of minimum enthalpy of reaction and formation of its potent precursor D7. Coupling of 2-CTP with 2-chlorothiophenoxy favours the formation of Pre D1, which acts as a direct precursor of intermediate D7, owing to the low activation energy of TS1 in Fig. 4.

Acknowledgment: This study has been supported by a grant of computing time from the National Computational Infrastructure (NCI), Australia (Project ID: De3). T.D. thanks the University of Newcastle, Australia for a postgraduate research scholarship.

References

1. Y. Ohashi, K. Yamada, I. Takemoto, T. Mizutani, K. Saeki (2005) *Biological and Pharmaceutical Bulletin* 28:1221–1223.
2. R.J. Laufer (1964) U.S. Patent 3,331,205.
3. R. Navarro, K. Bierbrauer, C. Mijangos, E. Goiti, H. Reinecke (2008*) Polymer Degradation and Stability* 93:585-591.
4. J.Q. Shi, J. Cheng, F.Y. Wanga, A. Flamm, Z.Y. Wang, X. Yang, S.X. Gao (2012) *Ecotoxicology and Environmental Safety* 78:134–141.
5. T. Benz, H. Hagenmaier, C. Lindig, J. She (1992) *Fresenius Journal of Analytical Chemistry* 344:286-291.
6. S. Sinkkonen, J. Koistinen (1990) *Chemosphere* 21:1161-1171.
7. S. Sinkkonen (1997) *Chemosphere* 34: 2585-2594.
8. S.L. Huntley, R.J. Wenning, D.J. Paustenbach, A.S. Wong, W.J. Luksemburg (1994) *Chemosphere* 29:257-272.
9. S. Nakai, S. Kishita, Y. Nomura, M. Hosomi (2007) *Chemosphere* 67:1852–1857.
10. S.Sinkkonen (2000) *New Types of Persistent halogenated Compounds, Springer* 3:289-314.
11. J. Czerwiński (2008) *Archives of Environmental Protection* 34:169-181.
12. S. Sinkkonen (1998) *Toxicological and Environmental Chemistry* 66: 105-112.
13. M.J. Frisch, G. Trucks et al. (2004) *Gaussian 03,* revision C.02 Gaussian, Inc.:Wallingford, CT.
14. A. Becke (1993) *Journal of Chemical Physics* 98:5648-5652.
15. M. Altarawneh, T. Dar, B. Z. Dlugogorski (2012) *Journal of Chemical & Engineering Data* (in press, dx.doi.org/10.1021/je3003173).
16. M. Altarawneh, B.Z. Dlugogorski, E.M. Kennedy, J.C. Mackie (2007) *Journal of Physical Chemistry A* 13:2563-2573.