The Effect of Hydrocarbons on PCDD/F Formation in the Gas-Phase Oxidation of 2,4,6 Trichlorophenol

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Abstract

The formation of tetrachlorinated dibenzo-p-dioxins (TCDD) and tetrachlorinated dibenzofurans (TCDF) were observed from the fuel lean gas-phase oxidation of 2,4,6 trichlorophenol (TCP) in the presence of hexane. The addition of hexane to the reaction mixture resulted in the previously unobserved formation of TCDF and a decrease in the yield of TCDD. Chemical analysis revealed the formation of two TCDFs and two TCDDs isomers in equal concentration. Mechanistic analyses of possible reaction pathways revealed that only the pathways involving formation from a pentachlorodiphenyl ether and a hydroxy pentachlorodiphenyl ether could explain the observed isomer distribution for TCDF and TCDD, respectively. Formation of TCDF from TCDD intermediates were shown to be inconsistent with the isomer distribution of TCDF. Steady state kinetic analyses were used to demonstrate that the formation of TCDF was the result of Cl abstraction from the pentachlordiphenyl ether by an increased pool of H, followed by inter-annular Cl displacement and ring closure. The decrease in TCDD was attributable to the quenching of phenolic radical intermediates by abstraction of H from hexane.

Introduction

The origin of PCDD/F continues to be a cause of considerable controversy[1-4]. A singular isuue is the importance of *de novo* versus precursor condensation on flyash surface. Gas-phase formation of PCDD/F is generally disregarded mainly because of Shaub and Tsang's[5] kinetic analysis. Shaub and Tsang performed steady state analysis of 13 reactions and concluded that gas-phase PCDD/F formation rates were too slow to account for incinerator emissions of PCDD/F. To verify Shaub and Tsang's kinetic analysis, we studied [6] the gas-phase reactions of 2,4,6 trichlorophenol (TCP) in a reaction atmosphere of dry air, and found that the major organic products were the 1,3,6,8 and 1,3,7,9 isomers of tetrachlorodibenzo-p-dioxin (TCDD). These two TCDD isomers were formed in equal yields with a maximum total yield of 0.1 % at 600 °C. Lesser quantities of dichlorodibenzo-p-dioxins were observed but no polychlorinated dibenzofurans were evident. The observed maximum yields of PCDD and the temperature of their formation was readily accounted for using the mechanism proposed by Shaub and Tsang if activation energy of rxn. 1 was decreased from 26 kcal/mol to 19.5 kcal/mol.


(Rxn. 1)
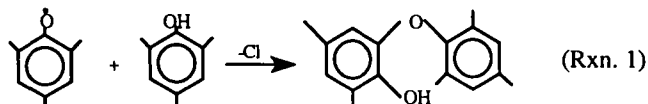
In contradiction to Shaub and Tsang results, simple calculations used to extrapolate our experimental results to field conditions indicated that the yields of PCDD formation via the gas-phase pathway could rival the yields calculated by other researchers for surface catalyzed condensation reactions.

These results generated a reconsideration of the kinetics of rxn. 1. Grotheer and Louw [7] studied rxn. 1 using chlorobenzene (PhCl) as a model substitute for chlorophenol and produced phenoxy radical (PhO•) by slow combustion of phenol.

$$PhO• + PhCl ----> Cl• + PhOPh \quad (Rxn. 2)$$
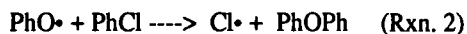
In these experiments, they observed the formation of dibenzofuran without the formation of diphenyl ether as would be predicted by rxn. 1. To account for these observations, they proposed an alternative reaction of phenoxy and chlorophenols as presented in scheme 1. In this pathway phenoxy tautomerizes to form the keto-resonance structure which then forms a reactive ether by radical-radical recombination. They propose that this pathway is preferred for all chorolphenols. Based on thermochemical calculations, they propose that the activation energy of rxn.1 is 24.5 kcal/mol versus the 19.5 kcal/mol deduced from our experiments. Because rxn. 1 is to slow to account for our observed PCDD yields using the higher activation energy, they propose a new scheme based on radical-radical recombination as shown in scheme 2.
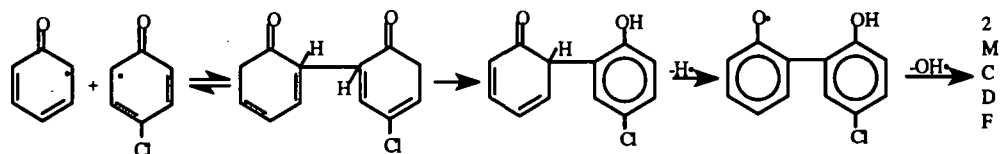
Scheme 1.   Born-Mulder-Louw PCDF formation mechanism. [8]
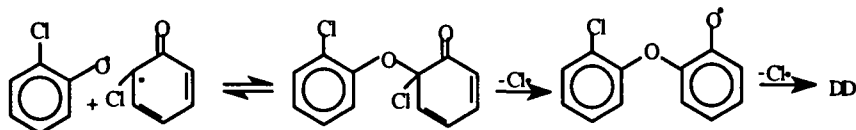
Scheme 2.   Born-Mulder-Louw PCDD formation mechanism.[8]

In scheme 2, a chlorine abstraction is required which is highly dependent on the concentration of the radical pool. We calculated equilibrium radical concentrations for our experiments using STANJAN computer code. We found that concentration of H• (which is far more reactive towards Cl abstraction than O or OH) was of the order of 10^{-18} mol/cc at 600°C, which makes chlorine abstraction and thus overall rate of scheme 2 too slow to account for our experimental PCDD yields. However, as the temperature is increased the concentration of the radical pool increased dramitically opening new reaction channels. Scheme 1 is also not applicable to our experimental results because tautomerization is invoked in the PCDF formation route, ortho-hydrogens must be available for this pathway to be feasible.[9] However in our experiments with 2,4,6 TCP, the ortho- sites are occupied by chlorine. Thus for PCDF formation to occur by scheme 1 for 2,4,6 TCP, these chlorines must be replaced by hydrogen. This does explain absence of PCDF in our experiments. Based on the absence of PCDF in our study and the results of Louw studies [7,8], it became evident that hydrogen or hydrocarbon radicals may play an important role in gas-phase PCDD/F formation. To test this hypothesis, we decided to repeat our experiments with a hydrogen source. Hence, our reactant mixture for present study consisted of 15 ppm TCP, 300 ppm hexane, and 4% O_2 in pure N_2.

Experimental

All experiments were conducted using our System for Thermal Diagnostic Studies (STDS). The STDS is a high-temperature flow reactor equipped for in-line product detection and identification using gas-chromatograpy (GC) in conjunction with mass-spectrometry (MS) and flame ionization detection (FID). For the gas-phase experiments reactor compartment holds a 1 cm

i.d. fused silica reactor. This reactor has been completely characterized as part of earlier studies [10]. From these studies it was concluded that results for experiments with chlorinated hydrocarbon were most consistent with homogeneous, gas-phase decomposition and reactions. In these studies, it was also shown that the reactor provided a narrow residence time distribution (t_r = 2.0 s ±1sigma = 0.2 s) and minimal thermal end-effects.

Samples of 5 % TCP in hexane solution were injected into the insertion region of the STDS using a calibrated syringe pump. The vaporized sample was mixed with a flowing gas of 4 % O_2 in N_2 in the insertion region, resulting in a reactor concentration of 15 ppm TCP, 300 ppm hexane, and 4 %O_2. The injection rate of the TCP/hexane mixture was varied such that a constant reactor inlet concentration of reactants was achieved at each experimental temperature.

The STDS was also modified to provide additional concentration and separation of the reactor effluent in order to provide a sufficiently concentrated sample for trace analysis of PCDD/F. An in-line Silico steel trap was added between the high-temperature reactor and the inlet to the GC. The trap was kept at 70°C during an experimental run, this allowed the heavier products (e.g., PCDD/F) to be adsorbed in the trap and the lighter products to be purged from the system. The heavier products were then thermally desorbed on to the GC column. This procedure was necessary to prevent overloading of the GC column with the large volume of sample that was generated.

The higher molecular weight compounds containing the PCDD/F were then swept into a DB-5, 30 m, 0.25 micron film thickness, 0.25 i.d. capillary column held at a trapping temperature of 70 °C. The GC was temperature programmed for 70 to 290 °C (10 minute hold) at 10 °C/min. Both scanning and selected ion monitoring (SIM) modes were used to detect and identify PCDD/F congener. The M^+ and $M+2^+$ ion for each congener class were monitored in the SIM mode and the correct ratio was used to confirm the identification of the congener.

Results
The results for this study are shown in figure 1. From 300 to 600 °C roughly constant 0.0014 % yields of 1,3,7,9 and 1,3,6,8 TCDD were observed with yields declining to 0.0002 % by 800 °C (lesser yields of a penta-CDD isomer were also observed). These are the same products as observed in the previous experiments with TCP without hexane. However in the current experiments, the maximum yields are a factor of 50 lower. It is also interesting that formation was observed at 300 °C. This is 100 °C lower than for the previous experiments and is attributable to the lower temperature initiation of decomposition of TCP by the radicals (peroxy) formed from the reactions of hexane and O_2. The formation at 300°C is in the temperature range where PCDD/F have been reported for heterogeneous experiments. This suggests that some of the conclusions reached in experiments, where the role of gas-phase and gas-surface reactions are poorly defined, may be in error.[1]

Somewhat surprisingly, formation of two tetrachloro- isomers of dibenzofuran (TCDF) were also observed over the entire temperature range with equal yields of 0.005 % at 700 C. No PCDFs were observed in the previous experiments without hexane. With hexane, the yields of TCDF actually exceeded the yields of TCDD (lesser yields of a di-CDF isomer (0.002%) were also observed). Formation of TCDF closely followed the decomposition of both TCDD and TCP.

Discussion
When considering the mechanism of formation of PCDF, the first question that arises is why they were formed at all, considering that they were not formed in the absence of hexane. Since the increase in yield of TCDF coincided with the decomposition of both TCP and TCDD, one also might question whether the formation of TCDF proceeds through a TCDD intermediate.
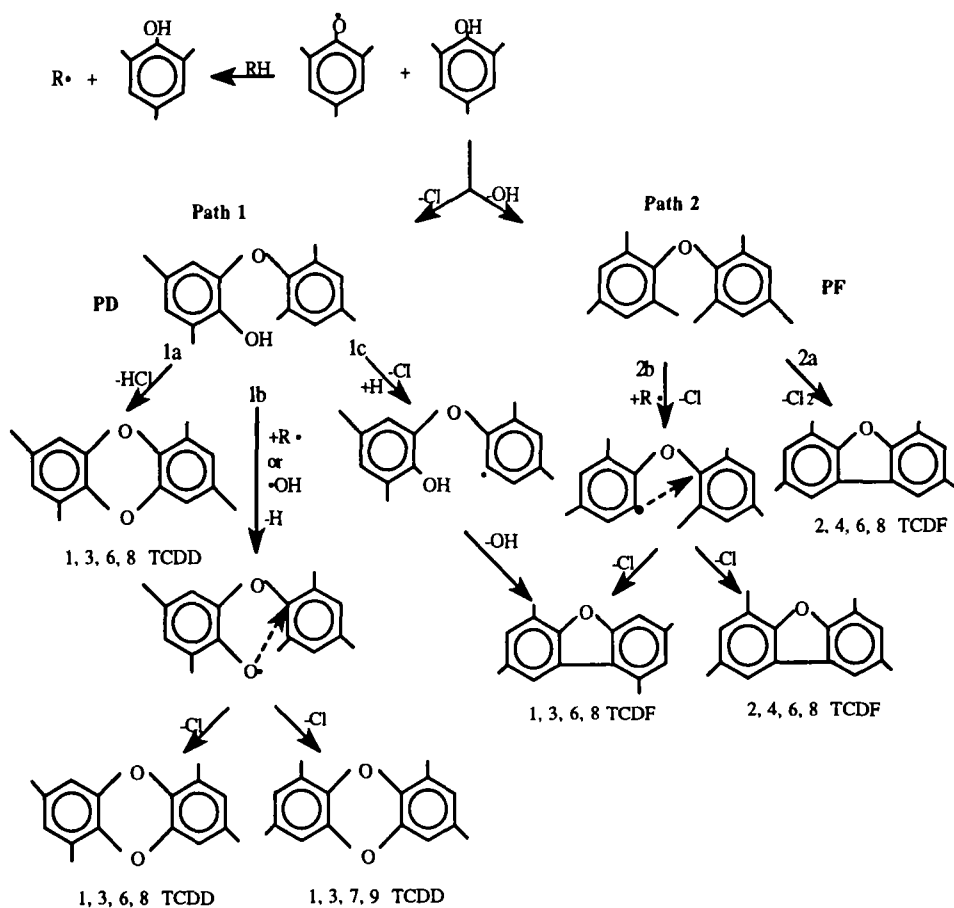
Scheme 3. TCDD and TCDF formation mechanisms based on this study.

We have previously shown that formation of TCDD from TCP is experimentally and theoretically consistent with formation through a hydroxydiphenylether, so-called predioxins (PD) (c.f. Scheme 3). This is because of the ease with which the phenolic hydrogen is abstracted (by OH or Cl) or unimolecularly dissociated and the relatively facile nature of inter-annular chlorine displacement.(pathway 1) The ease of chlorine displacement by phenoxy has been questioned by Grotheer and Louw [7]; however, presence of chlorine on all ortho sites and slow chlorine abstraction due to low hydrogen radical concentrations leaves chlorine displacement as the only viable option.

In our previous study, two possible mechanisms of TCDD formation from PD were identified: inter-annular HCl elimination (reaction 1a) and phenolic hydrogen abstraction followed by Cl displacement through a common intermediate (reaction 1b). The former reaction results in the formation of a single isomer of TCDD, while the latter results in the formation of two isomers. Because two isomers, in equal concentration, were observed experimentally, we proposed that 1b was the mechanism of formation of TCDD.

When one also considers formation of TCDF in addition to TCDD, a number of other potential pathways involving different radical and molecular intermediates must be included. The

primary perturbation of hexane on this system is the increased concentration of H and OH with the concomitant reduction in Cl. Cl and OH are expected to undergo similar reactions, primarily exothermic abstraction of H. H atoms on the other hand undergo exothermic reactions with Cl, including Cl abstraction and displacement. Reaction of OH and Cl with Cl are not favorable as they are usually endothermic. Thus it is logical to consider reaction pathways in the hexane containing system that involve H atoms. As will be shown below, reactions involving H favor formation of PCDF over PCDD.

Pathway 2 in scheme 3 involves initial formation of a diphenyl ether via displacement of OH by phenoxyl radical. This is contrast to pathway 1 which involved Cl displacement by phenoxy. The two pathways are always present and competing in essentially every system containing chlorophenol. The diphenyl ether can be dubbed a "pre-furan (PF)" because it can be readily converted into a dibenzofurans via various mechanisms.

In pathway 2a, TCDF is formed by inter-annular Cl_2 elimination. In pathway 2b, TCDF is formed by a slightly more complex pathway. First, Cl is abstracted (primarily by H). Interannular Cl displacement through a common intermediate follow to form TCDF. These pathways for formation of TCDF from PF are formally analogous to the mechanisms invoked for TCDD formation from PD. However in contrast to HCl elimination from PD, Cl_2 elimination from PF is not energetically favorable. Also in analogy to TCDD formation form PD, scheme 2a results in formation of only one TCDF isomer while reaction 2b can form two isomers. It is also possible to form a single isomer of TCDF from PD via pathways 1c. In this mechanism, Cl is abstracted from PD by H• followed by interannular displacement of OH to form TCDF. This pathway doesnot become important until 700°C when H• concentration increases by three orders of magnitude.

In addition to these pathways, it is also possible to draw feasible pathways to TCDF through the two TCDD isomers. These pathways involve H addition to break one of the ether linkages, followed by displacement of OH. The symmetry of the 1,3, 6, 8 TCDD isomer allows only the single 1, 3, 6, 8 TCDF isomer to be formed. However from 1, 3, 7, 9 TCDD, both the 2,4,6,8 and 1,3,7,9 TCDF isomers can be formed.

Thus the formation of TCDF from two TCDD isomers results in formation of three TCDF isomers. Only pathway 2b is consistent with the experimental observation of two TCDF isomers. Comparison of the preferred pathways for TCDD and TCDF formation, viz. 1b and 2b respectively, also suggest how the presence of hexane effects the total yield of TCDD/F and the TCDF to TCDD ratio. The hexane acts as a source of hydrogen. It provides the hydrogen necessary for Cl abstraction to form TCDF via pathway 2b, thus increasing the TCDF to TCDD ratio. Hexane also limits the formation of both the PD and PF precursors by adding a competing pathway. Phenoxyl can be readily converted back to phenol by abstraction of H from hexane. The proposed pathway are thus qualitatively consistent with the observed isomer distribution, the TCDF to TCDD branching ratio, and the trends in yields of total TCDD/F.

Our results, which suggest that chlorophenols form hydroxy diphenyl ethers by chlorine displacement and Louw's results, which were interpreted to suggest that chlorophenols form dibenzofurans by radical-radical recombination, may at first appear incongruous. However, closer examination reveals that Louw's mechanism is only valid for chlorophenols possessing an ortho-hydrogen, whereas only ortho-chlorines are present in 2,4,6 TCP. In fact, the vast majority of experiments reported in the literature are for chlorophenols which contain at least one ortho-chlorine.[1,2,8] This favors the formation of the hydroxy diphenyl ether and PCDD for conditions where the H concentration is low.

The formation of only PCDD from chlorophenols has been used to discount chlorophenols as a major source of PCDD/F in incinerator effluents. However, our results in conjunction with those of Louw suggest that their role may be significant. Less chlorinated (ortho-hydrogen containing) phenols are expected to occur predominately in full-scale combustors. Furthermore,

even when there is a source of highly chlorinated (ortho-chlorine containing) phenols, displacement of chlorine by hydrogen can create ortho-hydrogen containing chlorophenols or hydrogen can abstract chlorine from hydroxydiphenyl ether intermediates and form PCDF by Louw's and our mechanisms, respectively. Based on this re-investigation of the role of chlorophenols in PCDD/F formation, additional studies of the mechanism and kinetics of their reactions appear to be warranted.

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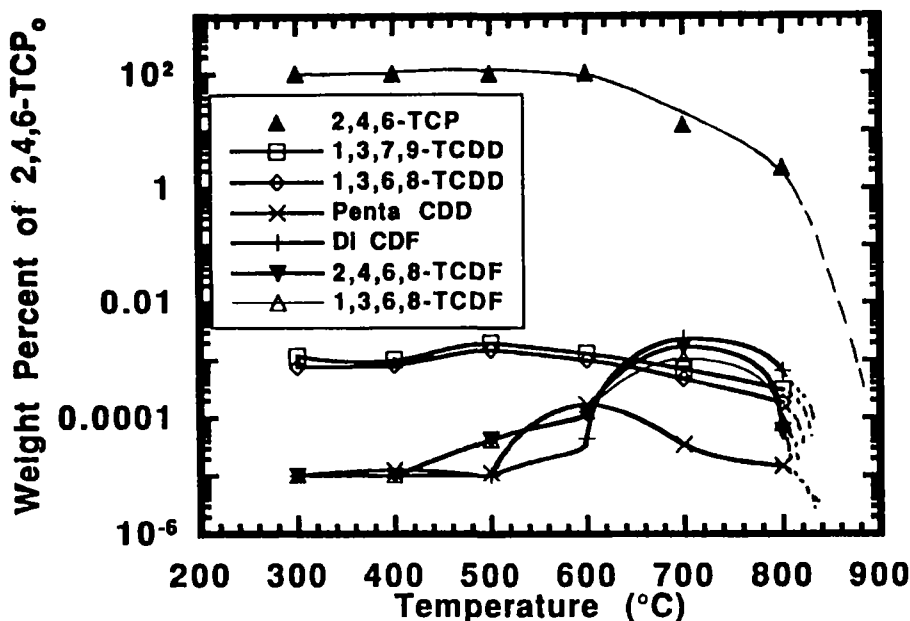10.   Rubey, W.A., and Grant, R.A., *Rev. Sci. Instrum.* 59: 265 (1988).

Figure 1.0   Gas-phase 2,4,6-TCP decomposition profile and PCDD/F formation profile [TCP]$_0$ = 15ppm, [Hexane]$_0$ = 300ppm, [O2]$_0$ = 4%, R.T. = 2.0 sec.