

Studies on Vapor Phase Phototransformation of Polychlorinated Dibenzo-*p*-Dioxins (PCDDs): Effect of Environmental Parameters

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1. Introduction

The release of PCDDs and PCDFs from a variety of combustion sources has been confirmed by a number of research groups¹⁻⁵. This release of highly toxic compounds is a matter of public and scientific concern and is reflected by the growing number of publications in the area over the past several years⁶⁻¹⁰. The concern has been heightened by a recent draft report on reassessment of dioxin health risks issued by the US Environmental Protection Agency (EPA). The report points out that dioxins are a probable cause of cancer and other adverse health effects such as the disruption of regulatory hormones, disorders in the reproductive and immune systems and abnormal fetal development¹¹.

Major dioxins produced from the incineration processes are hexa and octachloro dibenzo-*p*-dioxins (HxCDD and OCDD)¹²⁻¹³. The transformation of these congeners into congeners with higher toxicities through reductive dechlorination can affect calculations of toxic equivalent quantities (TEQ)¹⁴. Such transformations have been shown to occur in the solution phase¹⁵⁻¹⁸. It has been observed that both the rate of photodegradation and the nature of the photoproducts in solution phase and on bulk solids are affected by the physical state of the matrix. Significant differences have been observed in the types of dechlorination products formed in solution phase and on solid particles. A preferential loss of chlorines from the lateral positions (2,3,7,8) has been reported in solution phase studies¹⁵⁻¹⁸. However, Kieatiwong *et al* have observed that dechlorination of octachloro dibenzo-*p*-dioxin (OCDD) adsorbed on soil occurs preferentially at the peri (1,4,6,9) positions¹⁹. Similar results have been obtained by Tysklind *et al* with PCDD-bearing fly ash samples. Surprisingly, dechlorination of PCDFs, in the same study, was shown to occur preferentially at the lateral position²⁰. In contrast to the solution phase, Sivils *et al* have reported that, in the gas phase, congeners with peri substituted chlorines degrade at a faster rate²². It is apparent that, since the toxicity of PCDD is dependent on the chlorine substitution, the media can have significant effect on toxicities of photo irradiated PCDDs. While solution and solid phase phototransformation have been studied extensively, phototransformation of PCDDs in the vapor phase have been examined to a very limited degree, and only two studies have been reported on the subject in the open literature^{22,23}.

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The primary reason for the lack of information in this area is related to the low ambient vapor pressure of these compounds. However, it is quite evident that, despite their low vapor pressure, substantial portions of PCDD in the troposphere exist in the vapor phase; e.g., according to one estimate, ~20-60% of TCDD in this strata is present as the vapor²⁴. These facts, coupled with the observation that bioavailability of dioxins through pulmonary uptake is nearly 100 percent²⁵, make vapor phase photochemistry of dioxins an important and interesting area of research.

2. Experimental

The objective of the study was to investigate phototransformation of PCDDs in the vapor phase. The emphasis was placed on degradation kinetics of dioxins with varied chlorine substitutions and characterization of photoproducts obtained under different environmental conditions. These objectives were met with the application of a dual column chromatographic system interfaced to a photoreactor. A schematic of the experimental set-up is given in Figure 1. Details of the set-up have been provided in an earlier publication²².

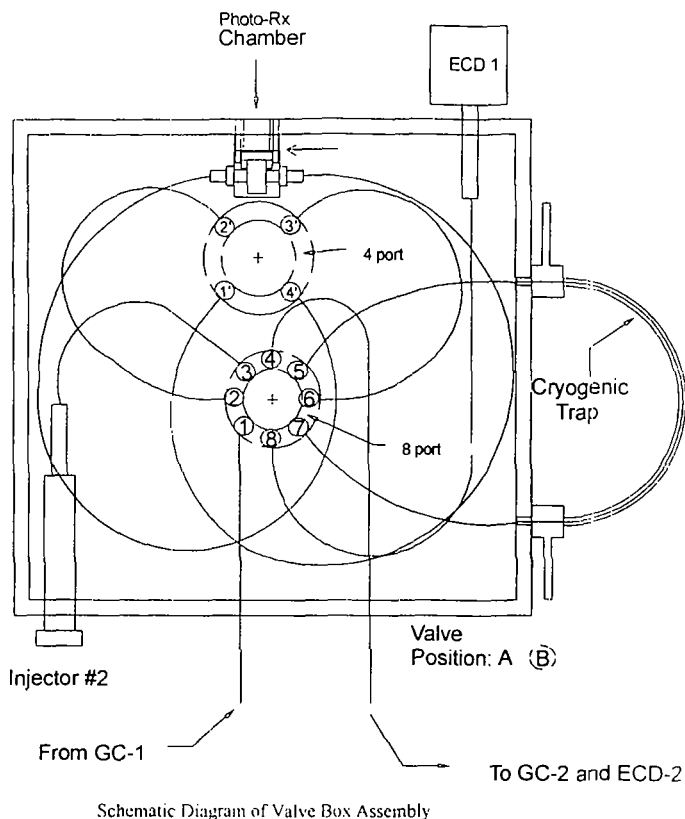


Figure (1)

The photoreactor consisted of a 500 microliter quartz cell placed in gas-tight stainless casing. The broadband UV excitation used for irradiation was obtained from a xenon arc lamp. To remove IR components, the light from the xenon lamp was made to pass through a water filter. The filtered light was collected and focused with a fiber optic coupler onto a high grade fused silica fiber optic bundle.

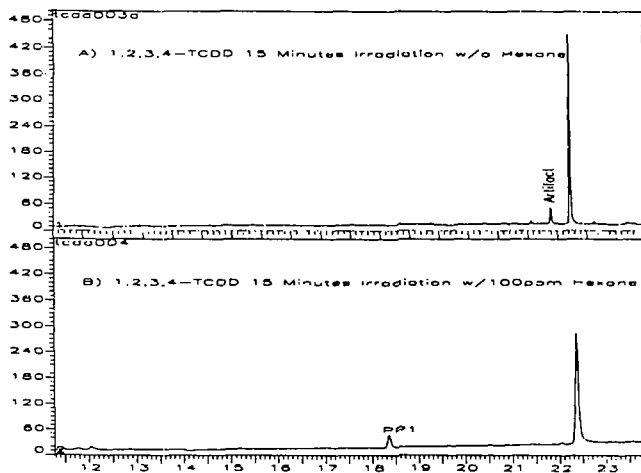
The gas chromatographic separation of analytes in the first gas chromatograph (GC-1) was achieved with a 15m x 0.25mm (i.d.) fused silica capillary coated with 95% methyl/5% phenyl polysiloxane. The separation of the residual analyte and hydrodehalogenation photoproducts was accomplished in the second gas chromatograph (GC-2) with a 30m x 0.25mm (i.d.) fused silica column coated with methyl/phenyl polysiloxane stationary phase. Helium (He) was used as the carrier gas in both gas chromatographic systems. It should be pointed out that the exact composition of carrier gas in the GC-1 was dependent on the gas composition for the photoirradiation experiments. Certified mixtures of selected gases in helium were used for the purpose, and these gas mixtures were obtained from Matheson, Inc., Joliet, Illinois.

3. Results and Discussion

Our earlier study on phototransformations of PCDDs in the vapor phase indicated that the transformation rate was appreciably higher for congeners with chlorine substitutions at the peri (1,4,6,9) positions than those with substitutions at the lateral positions (2,3,7,8)²². These studies were conducted in a 'clean' helium atmosphere with a fixed geometry photoreactor and did not permit elucidation of surface effects or the effects of gas composition. The present study was initiated to overcome these limitation. The objectives of the present experimentation were to investigate the effects of available surface and the presence of other chemicals that are likely to be present in the incinerator flue gases and in the ambient atmosphere. Of particular interest in this context was to observe the correlation, if any, between the formation of hydrodehalogenation photoproducts and the presence of hydrocarbon hydrogen donors. It should be pointed out that no such products were detected in the previous studies^{22,23}. Irradiation experiments conducted during the present study showed that the formation of hydrodehalogenation was significantly enhanced by the presence of hydrocarbons in the gas stream. The effect is shown graphically in Figure 2, which depicts chromatographic traces of residual TCDD and photoproducts in the presence of 100ppm of hexane in helium. The mass spectra and the chromatographic retention time of photoproduct matched that of 1,2,3 trichloro-*p*-dibenzo indicating a preferential loss of the peri chlorines from the 1,2,3,4 TCDD molecule. A correlation between hydrocarbon concentration and amount of photoproduct was, however, not established. A subsequent timed exposure experiment showed the concentration of the 1,2,3 TriCDD increased initially but declined with continued irradiation. A graphical representation of formation and subsequent disappearance of 1,2,3 TriCDD is presented in Figure 3. The process can be expressed mathematically through the following equation:

$$[C] = [A_0] \left[1 - \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} + k_1 e^{-k_2 t}) \right] \quad [1]$$

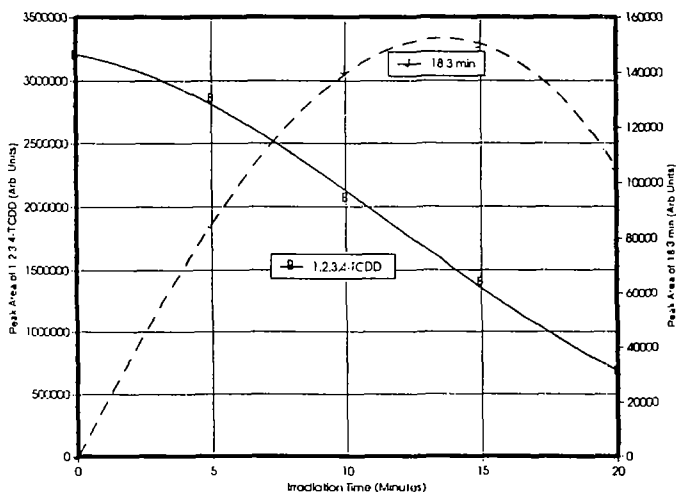
where C is concentration of 1,2,3 TriCDD
 A₀ is the initial concentration of 1,2,3,4 TCDD
 k₁ is the rate constant for formation of TriCDD
 k₂ is the rate constant for disappearance of 1,2,3 TriCDD



Chromatographic Profiles of 1,2,3,4-TCDD Irradiated in the Presence of Hexane. The artifact in trace A is due to an impurity which was present even with no irradiation.

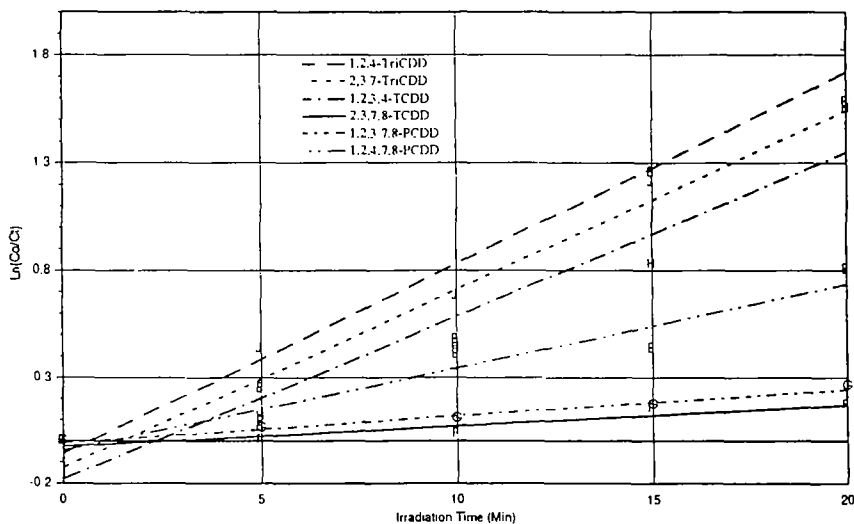
Figure (2)

The evidence for preferred phototransformation of PCDD at the peri substitution was also evident from the first order treatment of transformation data for selected PCDDs. The data showed that degradation rate generally decreased with an increase in number of chlorines. In congeners with the same number of chlorines, the ones with higher numbers



Graphical Representation of 1,2,3,4-TCDD Degradation vs. Photoproduct Formation as a Function of Irradiation Period.

Figure (3)



Graphical Representation of Photodegradation of Selected PCDDs With Hexane Dopant.

Figure (4)

of peri chlorines degraded faster (Figure 4). It is interesting to note that the congener with highest toxicity and no peri chlorines, namely the 2,3,7,8 TCDD, transformed at the slowest rate. This is a complete reversal of the results obtained in the solution phase.

A significant increase in the degradation rate of all PCDDs was observed in the presence of oxygen. The increase can be attributed to conversion of oxygen to ozone under the experimental conditions used in the study. Ozone is a powerful oxidizing agent and can lead to the formation of peroxide. The increase in phototransformation rate could not be directly correlated with oxygen concentration over the concentration range used in the present study.

A small but discernable increase in the photodegradation rate was also observed in the presence of water. This increase can be attributed to the formation of reactive hydroxyl radicals (OH^*) which can attack the parent PCDD. The effect was monitored with selected trichloro to pentachloro congeners. The results indicated an increase in photodegradation rate of all PCDD tested. However, the trends were similar to those observed with 'pure' helium.

4. Conclusions

The data obtained from the present study indicated that photodechlorination in gas phase occurred preferentially from the peri position. This conclusion was drawn on the basis of the relative rates of disappearance of the analyte and photoproducts. The degradation rate for 2,3,7,8 TCDD (which possesses no peri chlorines) was measurably slower than all trichloro through pentachloro congeners. The data seem to indicate that, in the vapor phase, the more toxic laterally substituted congeners degrade at a slower rate than the peri substituted congeners.

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6. References

- 1) I. Fangmark, B. Stromberg, N. Berge and C. Rappe, *Environ. Sci. Technol.*, 28(4) (1994) 624-629.
- 2) R.R. Bumb, *Science*, 210 (1980) 385.
- 3) C.C. Travis and H.A. Hattermer-Frey, *Risk Anal.*, 9 (1989) 91.
- 4) K. Ballschmiter, H. Buchert, A. Niemczyk, A. Munder, M. Swerev, *Chemosphere*, 15 (1986) 901-915.
- 5) H.Y. Tong and F.W. Karasek, *Chemosphere*, 15 (1986) 1219-1224.
- 6) H. Buchert and K. Ballschmiter, *Chemosphere*, 15 (1986) 1923-1926.
- 7) K. Schiedl, F. Wurst, R.P. Kuna, *Chemosphere*, 15 (1986) 2089-2092.
- 8) R.E. Clement, H.M. Tosine, J. Osborne, V. Ozvacic, G. Wong and S. Thornedyke, *Chemosphere*, 16 (1987) 1895-1900.
- 9) J.R. Vasalli, *J. Air Pollut. Control Assoc.*, 37 (1987) 1451-1463.
- 10) H.Y. Tong, S. Arghestani, M.L. Gross and F.W. Karasek, *Chemosphere*, 18 (1989) 577-584.
- 11) B. Hileman, *C&EN*, 72(38) (1994) 6-7
- 12) L. Dickson and F. Karasek, *J. Chromatogr.*, 1987, 389, 127-137.
- 13) K. Bruce, L. Beach and R. Gullet, *Waste Management*, 1991, 11, 97-102.
- 14) S. Safe, *C.R.C. Crit. Rev. Toxicol.*, 1990, 21, 51-88.
- 15) R. Atkinson, *The Science of the Total Environment*, 104 (1991) 17-33.
- 16) J.R. Plimmer, M.I. Klingebiel, D.G. Crosby and A.S. Wong, *Adv. Chem. Ser.*, 120 (1971) 44-54.
- 17) M. Dung and P. O'Keefe, *Organohalogen Compounds*, 8 (1992) 233-236.
- 18) Q. Yan, L.D. Sivils, S.D. Palepu, S. Kapila, A.F. Yanders, A.A. Elseewi, *Chemosphere*, 29 (1994) 2183-2192.
- 19) S. Kieatiwong, L.V. Nguyen, V.R. Hebert, M. Hackett, G.C. Miller, M.J. Mille and R. Mitzel, *Environ. Sci Techno.* 24 (1990) 1575-1580.
- 20) M. Tysklind, A. Carey, C. Rappe and G. Miller, *Organohalogen Compounds*, 8 (1992) 293-296.
- 21) M. Tysklind, K. Lundgren, C. Rappe, L. Erikson and M. Sjoström, *Organohalogen Compounds*, 8 (1992) 173-175.
- 22) L.D. Sivils, S. Kapila, Q. Yan and A.A. Elseewi, *J. Chromatogr.*, in press.
- 23) R. Orth, C. Ritchie and F. Hileman, *Chemosphere*, 1989, 18, 1275-1282.
- 24) T.F. Bidleman, *Environ. Sci. Technol.*, 32 (1988) 361-367.
- 25) C. Nessel, M. Amoroso, T. Umbreit, R. Meeker and M. Gallo, *Chemosphere*, 25 (1992) 29-32.