

Studies on Gas-Phase Phototransformation of Polychlorinated Dibenzo-p-Dioxins

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INTRODUCTION

Many sites in the United States and abroad are contaminated with polychlorinated dibenzo-p-dioxins (PCDDs) as a result of accidents or prolonged industrial activities. PCDDs, or dioxins (as these chemicals are generally known), are highly toxic unwanted byproducts of a number of chemical processes such as incineration and application of chlorine bleach in the pulp and paper industries¹⁻⁴. The 75 PCDD homologues show varied physicochemical properties and toxicities depending on the degree and position of chlorine substitutions. Analogs with four or more chlorines are practically insoluble in water, resistant to biodegradation and exhibit a high degree of environmental persistence^{5,6}.

Photodegradation, i.e., transformation achieved through exposure to the near UV components of sunlight, is reported to be the most significant natural mechanism for removal of dioxins in the environment⁷. The degradation proceeds through a free radical mechanism and, under suitable conditions, leads to the formation of analogs with fewer chlorines. Depending on the substitution, the elimination of chlorine can result in analogs with higher or lower toxicities⁸. A number of studies dealing with photodegradation of dioxins and related polychlorinated dibenzo furans (PCDFs) in the solution phase have been reported in literature⁹⁻¹⁵. However, the mechanism of photoreaction for these compounds has not been fully elucidated.

It has been observed that both the rate of degradation and the nature of photoproducts are affected by the physical state of the matrix. Significant differences have been reported in the types of dechlorination products formed in solution phase and on solid particles^{16,17}. A preferential loss of chlorines from the lateral positions (2,3,7,8) has been reported in a number of solution phase studies. However, Miller and coworkers have observed that dechlorination of octachlorodibenzo-p-dioxin (OCDD) adsorbed on soil occurs preferentially at the peri positions (1,4,6,9)¹⁸. Similar results have been obtained by Rappe and coworkers with PCDD bearing fly ash samples¹⁹. Surprisingly, dechlorination of PCDFs, in the same study, was shown to occur preferentially at the lateral position¹⁹. Since the toxicity of PCDD is dependent on the chlorine substitution, the dechlorination route can have significant effect on toxicity. A review of the literature revealed that one of the most overlooked areas has been photodegradation in the vapor phase.

The primary reason for the lack of information in this area is related to the low

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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 is present in the vapor form²⁰. Furthermore, one of the major sources of widespread distribution of dioxins in the environment is incineration which releases these contaminants into the atmosphere²¹⁻²³. These facts, coupled with the observation that bioavailability of dioxins through pulmonary uptake is nearly 100 percent²⁴, make gas phase photochemistry of dioxins an important and interesting area of research.

EXPERIMENTAL

The chromatographic system was constructed around a thermostated aluminum block. The block served as the housing for the photoreactor and two switching valves. An externally mounted cryogenically cooled trap was mounted to the side of the block. The gas chromatographs, photoreactor and the cryotrap were interconnected through the switching valves. A schematic of the system is shown in Figure 1. The analytes of interest were introduced into the system via the first gas chromatograph (GC-1) equipped with an electron capture detector (ECD-1). The detector served as a monitor for eluting components and facilitated in switching the appropriate component. The component transfers were accomplished with an eight port valve (V1). A four port valve (V2) was also incorporated into the system to permit transfer and entrapment of the selected analyte in the photoreactor. This feature allowed variation of irradiation time over a wide range. After irradiation, the residual analytes and photoproducts were transferred to the cryotrap and standard analytes could be added to the second injector to facilitate product peak confirmation through co-chromatography. All components of the system were interconnected with 0.25mm (id) aluminum clad fused silica tubing.

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. The light from the xenon lamp was passed through a water filter (Oriol 61945) to absorb IR radiation. The filtered light was collected and focused with a fiber optic coupler (Oriol 77800) onto a high grade fused silica fiber optic bundle (Fiberguide Industries SFS320/385T). The bundle was designed to withstand temperatures up to 325° C for extended periods of time.

Initially, both valves were switched to position A. This permitted passage of effluent from Column 1 to ECD-1 while bypassing the photoreactor. All valve switching operation timing began with the appearance of the solvent front at ECD-1. The change of V2 to position B allowed the sample band to pass into the photoreactor. After a set time interval, V2 was switched to position A, trapping the sample band in the photoreactor. The analyte in the reactor was irradiated with broadband radiation in the UV/visible region. After the desired exposure period, the reactor contents were transferred to the cryogenically cooled trap by switching V2 to position B. V1 was switched to position B, and the trapped residual analyte and photoproduct were flash vaporized and introduced into the second column. The separated components were monitored by the second ECD-2 or a quadrupole mass spectrometer. The initial separation of the analyte was carried out in GC-1 with a 15m x 0.25mm fused silica capillary column coated with 95% methyl/5% phenyl polysiloxane.

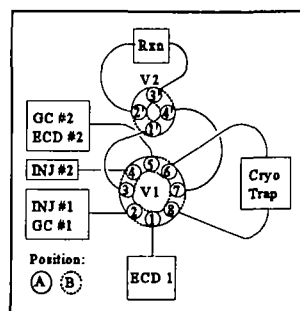


Figure 1. Schematic of 2-D GC system.

Separation of the residual and photoproducts was accomplished with a 30m x 0.25mm fused silica capillary column coated with 95% methyl/5% phenyl polysiloxane that was installed in GC-2 (Shimadzu MiniGC-3). The column oven parameters and chromatographic conditions were optimized for the analyte of interest.

RESULTS AND DISCUSSION

The overall objective of the present study was to investigate photoinduced disappearance (dechlorination) of polychlorinated dibenzo-p-dioxins in the gas phase. The specific objectives of the study were to determine the correlation between rate of disappearance and chlorine substitution and to characterize neutral photoproducts. A two dimensional gas

chromatography system with a photoreactor was selected as the apparatus of choice for the study. Prior to its use in PCDD studies, the performance of the system was evaluated with hexachlorobenzene (HCB). This polychlorinated compound was selected because of its high response with both ECD and mass spectrometer detectors as well as its good chromatographic properties. Chromatographic profiles of HCB obtained through peak transfer to the second GC are shown in Figure 2. The peak in profile A shows HCB transferred without irradiation whereas profile B depicts two peaks obtained after 5 minutes irradiation. One of the peaks in profile B eluted with the same retention time as HCB while the other eluted 2.94 minutes earlier than HCB. The retention time of the early peak matched that of pentachlorobenzene (PCB). A quantitative assessment of the photoreaction revealed that, under the experimental conditions, approximately 5% of HCB was converted to PCB. However, an increased yield of photoproducts was obtained when a hydrogen donor such as hexane was added to the gas stream.

In order to delineate a correlation between dioxin structure and photodegradation, a number of

trichloro through pentachloro dioxins were subjected to photoirradiation. The congeners selected for the study included 2,3,7 trichlorodibenzo-p-dioxin (TriCDD); 1,2,3,4 tetrachlorodibenzo-p-dioxin (1,2,3,4 TCDD); 2,3,7,8 tetrachlorodibenzo-p-dioxin (2,3,7,8 TCDD); 1,2,4,7,8 pentachlorodibenzo-p-dioxin (1,2,4,7,8 P₅CDD); and 1,2,3,7,8

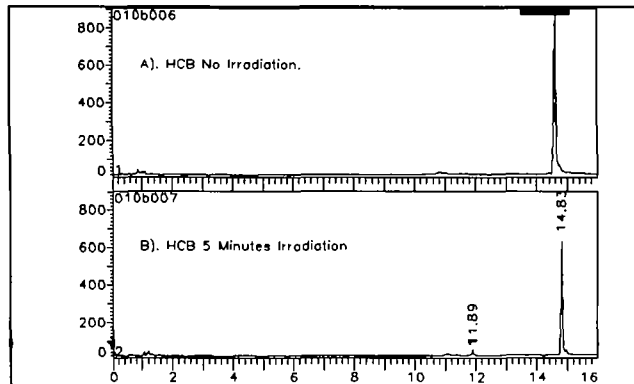


Figure 2. Chromatographic profiles of HCB. Chromatographic output for this and subsequent figures were obtained with ECD-2.

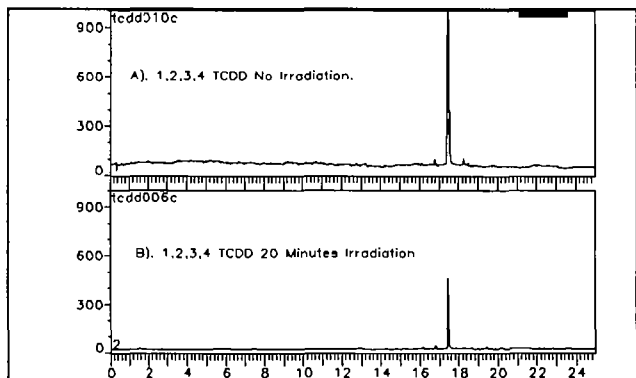


Figure 3. Chromatographic profiles of 1,2,3,4 TCDD

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pentachlorodibenzo-p-dioxin (1,2,3,7,8 P₅CDD).

The irradiation experiments revealed that different dioxin congeners degrade at different rates; e.g., a 20-minute irradiation resulted in degradation of as much as 80% of TriCDD while only 30% of the 2,3,7,8 TCDD was found to degrade under the same conditions. The results also showed that, in contrast to HCB, none of the dioxin congeners yielded a hydrodehalogenation photoproduct. The chromatographic output for 1,2,3,4 TCDD is shown in Figure 3. The upper trace represents non-irradiated analyte and the bottom trace depicts the residual analyte after 20 minutes of irradiation. These chromatographic results are typical of the profiles obtained with the other congeners. The rate of disappearance for different congeners was determined. An examination of the data revealed an inverse relationship between the degree of chlorination and the rate of disappearance. The data show that the trichloro congener degraded at a faster rate than the tetrachloro which, in turn, degraded faster than the pentachloro congeners. The data also showed that degradation followed first order kinetics.

The data obtained from the present studies indicated that photodechlorination occurred preferentially from the peri position, and the lack of photoproducts prevented an

i n d e p e n d e n t
confirmation of the
preferential loss
m e c h a n i s m .
Therefore, this
conclusion was
drawn only on the
basis of the
relative rates of
disappearance of
the analyte peak.
The degradation
rate for 2,3,7,8
TCDD (which
possesses no peri
chlorines) was
measurably slower
than all trichloro
t h r o u g h
p e n t a c h l o r o
congeners. Clear

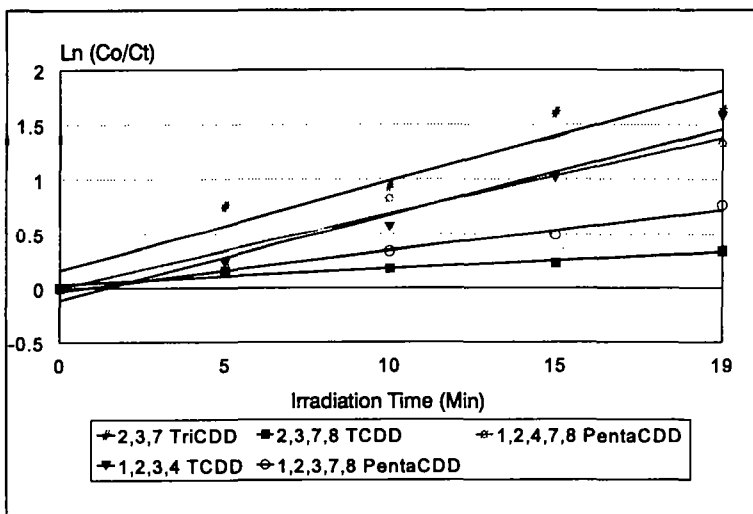


Figure 4. Overlay of PCDD plots.

differences were also obtained between the two pentachloro isomers. 1,2,4,7,8 P₅CDD with two peri (1&4) chlorines degraded faster than 1,2,3,7,8 P₅CDD which contains only one peri chlorine. These results are summarized in Figure 4. The data seem to indicate that the more toxic laterally substituted congeners degrade at a slower rate than the peri substituted congeners.

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