

Investigation Of The *De Novo* Process Using ^{13}C Amorphous Carbon

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Abstract

A series of experiments were performed to study the formation of organohalogen compounds under conditions described by other researchers, but using ^{13}C -enriched charcoal. Native and ^{13}C -labelled PCDD/PCDF were produced. The starting materials were subjected to a series of extractions and the experiments were repeated. The results from these experiments suggest that the major source of PCDD/PCDF production was organic precursor compounds adsorbed onto the particulate carbon.

Introduction

It is well established that polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran (PCDD/PCDF) formation in municipal waste incineration is in some way related to the catalytic activity of flyash towards precursor materials. The nature of the precursors remains a topic of considerable debate and several studies have been directed at the production of PCDD and PCDF from chemically related precursors such as chlorinated phenols¹ or through *de Novo* synthesis from unrelated compounds. In earlier studies it was suggested that elemental carbon in fly ash acts as an adsorbent to the precursor compounds² but more recently it was reported that the particulate carbon itself acts as the precursor³.

In this work, the role of particulate carbon in the *deNovo* synthesis of PCDD/F is further investigated through the use of ^{13}C -enriched amorphous carbon.

Experimental

Materials:

Carbon - ^{13}C , amorphous, 99 atom % ^{13}C was obtained from Aldrich Chemical Company Inc. Reagent grade Cupric Chloride, Dihydrate and Potassium Chloride were obtained from J.T. Baker Chemical company and BDH Inc, respectively. Flyash was obtained from Sunlakes, Arizona, USA. Solvents were of OmniSolv grade, purchased from BDH.

A reference standard containing all 210 isomers of native PCDD/PCDF and all

75 isomers of ^{13}C -labelled PCDD was prepared in our laboratories⁴.

Instrumentation:

An HP 5880 gas chromatograph equipped with flame ionization and electron capture detectors was used. The GC-MS system was an HP 5890/5970 MSD. The ion source temperature was 200°C and the MS was operated in electron impact selected ion monitoring (EISIM) mode. A minimum of 2 characteristic ions were monitored for each PCDD/F congener group containing 4 to 8 chlorines. The columns used were either DB-5 (30 m x 0.25 mm i.d.) obtained from J&W scientific, or a 20 m x 0.25 mm i.d. $D_1 = 0.20 \mu\text{m}$ liquid crystal column prepared in our laboratories⁵.

Experimental Procedures:

A 20g portion of fly ash (sieved, $<180\mu\text{m}$) was placed in a quartz flow tube and annealed for 12 hours in a horizontal oven at 500°C under an air stream of 50 mL/min. This process is said to remove and destroy volatile organics from the flyash³. A mixture of 15g of the annealed flyash, 0.155g of ^{13}C - carbon, 0.15g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.15g KCl was prepared. Two 2g samples were transferred to quartz flow tubes, and one was placed in a vertical oven at 300°C for 2 hours under an air flow of 45-50 mL/min. Both samples were extracted by column elution using 250 mL of toluene. A 2g sample of annealed flyash only was also extracted. All extracts were concentrated to a volume of 100 μL .

The remainder of unused annealed flyash (ca. 6g) and the flyash/ ^{13}C mixture (ca. 7g) were extracted as follows: In total 5 extractions were performed on each. Five x 30 mL toluene extracts, sonicated for 3.5, 2, 4, 1.5 and 1 hours, all at 50°C. The 5 extracts were combined and concentrated to ca. 100 μL .

The solids were left to air-dry and 1.5 grams of the ^{13}C -enriched flyash mixture was placed in a flow tube and extracted by column elution with 250 mL toluene followed by 200 mL of dichloromethane. This background extraction was concentrated and analyzed for pre-existing PCDD/F. The solid material was allowed to air dry and was then heated for two hours at 300°C under an air flow of 45-50 mL/min. Extraction by column elution with 250 mL toluene and concentration of the extract followed.

Results and Discussion

The results of the GC-MSD analyses for native and labelled PCDD/PCDF are given in Tables 1 and 2.

The conditions chosen for these experiments were as outlined by Stieglitz *et. al.*³ except that in our initial experiments no efforts were made to purify the carbon, and our annealing time to produce "carbon-free" flyash was twice as long. A single analysis of this annealed flyash showed the presence of native PCDD/PCDF (combined) totalling 47 ng/g. Analysis of the ^{13}C enriched flyash mixture gave slightly higher results, but analysis of the carbon alone gave no indication of PCDD/F. The mean values of these two experiments were thus taken as the background levels of the mixture.

Table 1 Amounts of native and ¹³C labelled PCDD (ng per gram)
nd = not detected, mixture = flyash, 1wt% ¹³C, 0.4wt% Cu(II), 1wt% KCl

sample	column	tetra	penta	hexa	hepta	octa	Total
annealed flyash	DB-5	Native: 5	nd	1	3	2	11
		Labelled: nd	nd	nd	nd	nd	nd
unheated mixture	DB-5	Native: 7	7	7	3	<1	24
		Labelled: nd	nd	nd	nd	nd	nd
heated mixture	liquid crystal	Native: 4	14	14	13	4	49
		Labelled: nd	8	11	16	15	50
¹³ C-Carbon	liquid crystal	Native: nd	nd	nd	nd	nd	nd
		Labelled: nd	nd	nd	nd	7	7
background for extracted mixture	liquid crystal	Native: nd	nd	nd	nd	nd	nd
		Labelled: nd	nd	nd	nd	nd	nd
extracted mixture heated	liquid crystal	Native: nd	13	15	8	5	41
		Labelled: nd	nd	nd	nd	nd	nd

Table 2 Amounts of native and ¹³C labelled PCDF (ng per gram)
nd = not detected, mixture = flyash, 1wt% ¹³C, 0.4wt% Cu(II), 1wt% KCl

sample	column	tetra	penta	hexa	hepta	octa	Total
annealed flyash	DB-5	Native: 6	9	13	7	1	36
		Labelled: nd	nd	nd	nd	nd	nd
unheated mixture	DB-5	Native: 17	16	11	3	<1	47
		Labelled: nd	nd	nd	nd	nd	nd
heated mixture	liquid crystal	Native: 22	31	32	24	10	120
		Labelled: 1	30	51	49	97	230
¹³ C-Carbon	liquid crystal	Native: nd	nd	nd	nd	nd	nd
		Labelled: nd	nd	nd	7	18	25
background for extracted mixture	liquid crystal	Native: nd	nd	nd	5	2	7
		Labelled: nd	nd	nd	nd	nd	nd
extracted mixture heated	liquid crystal	Native: 13	18	19	11	3	64
		Labelled: 1	4	7	5	6	23

Heating the mixture under the described conditions resulted in the production of native and labelled PCDD/F. The liquid crystal capillary column proved to be instrumental in permitting analysis without further clean-up of the extracts. This is discussed elsewhere⁵. The initial experiment yielded quantities of native PCDD/F that far exceeded the 1% contribution that would be expected from the isotopic impurity of the amorphous carbon. This raised the question of whether organic compounds had been adsorbed onto the particulate carbon from the ambient environment and/or from the manufacturing process of the amorphous material, and whether these adsorbed compounds were the actual source of precursors in the deNovo production of PCDD/F.

GC-FID analysis of the 5 combined extracts of the annealed flyash revealed many peaks, and a striking increase in total peak area was observed as a result of the addition of the 1 wt% of charcoal. Another series of successive extractions showed a gradual decrease in amounts of organics present, however changing the type of solvent showed a remarkable increase in the total peak areas obtained. Leaving the material exposed to ambient conditions also resulted in an increase in total peak area, suggesting that some organic compounds present in ambient air were adsorbed. This work indicated that it would be impractical if not impossible to exhaustively remove all extractables from the carbon and/or flyash. However, it was reasoned that if labelled PCDD/F formation stemmed from the presence of ¹³C enriched organic compounds that were originally present from the manufacture of the ¹³C carbon, their removal even if only to a limited degree, would result in a decrease in production of labelled PCDD/F. Indeed, comparison of results for labelled PCDD/F production from the extracted material versus those of the original experiment shows a drop in production by one order of magnitude. In contrast, approximately the same amounts of native PCDD/F were observed in both cases. These experiments suggest that the precursors for PCDD/F production are organic compounds that are adsorbed onto the particulate carbon.

References

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