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MECHANISM OF FORMATION OF POLYCHLORINATED DIBENZO-*p*-DIOXINS PRODUCED ON MUNICIPAL INCINERATOR FLYASH FROM REACTIONS OF CHLORINATED PHENOLS

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SUMMARY

All incinerators burning municipal waste produce chlorinated dioxins. The mechanism by which these compounds are formed is unknown. Experiments were performed that show these compounds can be produced from known precursors by surface catalysed reactions on the flyash particulates present in the incineration process. A full range of the tetra- through octachlorinated dibenzo-*p*-dioxins were produced from ¹³C-labelled pentachlorophenol and two trichlorophenols on the surface of flyash from an Ontario municipal incinerator that had been previously freed from organic material. A simple flow-tube apparatus at 300°C under a 10-ml/min nitrogen flow was used for the experiments. The use of ¹³C-labelled pentachlorophenol gave a direct measure of the extent of the catalytic reactivity of the flyash surface. Much lower amounts of chlorinated dioxins were produced in similar experiments with flyash from a modern Japanese incinerator whose effluents are normally extremely low in these compounds. Only small amounts of octachlorodioxin, the thermal condensation product expected, were formed using ground firebrick or an empty flow-tube for the reactive surface. These results indicate that the flyash surface has constituents and properties that promote the production of chlorinated dioxins from chlorinated phenols and support the catalyzed surface reaction mechanism previously proposed.

INTRODUCTION

The incineration of municipal refuse has become an attractive alternative to the practice of dumping refuse in landfill sites. Incinerating refuse in plants close to urban areas offers the advantages of low transportation costs, reduction in the volume of solid wastes and the possibility of energy recovery. However, the incineration of refuse and combustion processes in general emit potentially hazardous substances into the environment. In a review of organic compounds found in incinerator effluent, Junk and Ford¹ listed over 330 substances, including aliphatics, polynuclear aromatic hydrocarbons, substituted benzenes, carbonyl compounds and sulphur and nitrogen containing compounds.

Since 1977 when Olie *et al.*² discovered chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans in the effluent of a municipal incinerator in The Netherlands, attention has been focused on these toxic compounds. Chlorinated dioxins have since been found in flyash from incinerators located in Canada, Japan, Switzerland, France, Norway and the U.S.A.³⁻⁷. These compounds are of considerable public concern because certain isomers (*e.g.* 2,3,7,8-tetrachlorodibenzo-*p*-dioxin) are extremely toxic and can cause liver damage and chloracne⁸.

Discussions of thermal formation of dioxins have generally dealt with gas-phase reactions and extrapolation from the liquid phase to the gas phase. Three general mechanisms have been proposed: (1) survival of trace levels in the fuel; (2) generation from precursors such as chlorinated phenols; (3) *de novo* synthesis from chemically dissimilar compounds and sources of chlorine⁹.

However, reports by Shaub and Tsang¹⁰⁻¹² have made strong arguments in favour of heterogeneous gas-solid phase reactions as the source of chlorinated dioxins from incineration. Computer simulations based on models of homogeneous gas-phase mechanisms predict lower levels of chlorinated dioxins and chlorophenates than are found in incinerators¹¹. Therefore heterogeneous gas-solid reactions which have much more favourable kinetics than radical reactions at lower temperatures must be considered. Flyash has many Lewis and Brønsted acid and base sites. A chemisorbed precursor molecule could become very reactive, due to the removal of H or Cl from the bound molecule by fast abstraction by gas-phase radicals or by neighbouring reactive sites on the flyash¹². The activation of the phenol by adsorption, possibly through the hydroxyl group, could be similar to that seen by Sanderman *et al.*¹³ who reported that the pyrolysis of the sodium salt of pentachlorophenol gave much larger yields of octachlorodioxin than the pyrolysis of pentachlorophenol alone. Experiments using chlorinated dioxins adsorbed onto flyash have shown that gas-solid phase chlorination of dioxins is rapid and efficient¹⁴⁻¹⁷.

In this study chlorinated phenols were passed through a bed of municipal incinerator flyash at 300°C. Tetrachloro- through octachlorodioxin reaction products were detected in the flyash extract and downstream impinger.

EXPERIMENTAL

Chemicals and standards

Pentachlorophenol was purchased from Aldrich (Milwaukee, WI, U.S.A.). 2,4,5-Trichlorophenol and 3,4,5-trichlorophenol were purchased from Fluka (Caledon Labs., Georgetown, Canada). Unlabelled chlorinated dibenzo-*p*-dioxin standards were supplied by the Ontario Ministry of the Environment. ¹³C₁₂-labelled tetrachlorodioxin and octachlorodioxin were purchased from Cambridge Isotopes Labs. (Woburn, MA, U.S.A.) and labelled pentachlorophenol from MSD Isotopes (Dorval, Canada). All chemicals were 98% pur or better. All solvents were of "distilled-in-glass" grade (Caledon Labs). Chromosorb P Non-Acid Washed chromatographic support derived from crushed firebrick was purchased from Johns-Mansville (Denver, CO, U.S.A.).

Flyash

Flyash from a refractory-wall mass-burning municipal refuse incinerator in

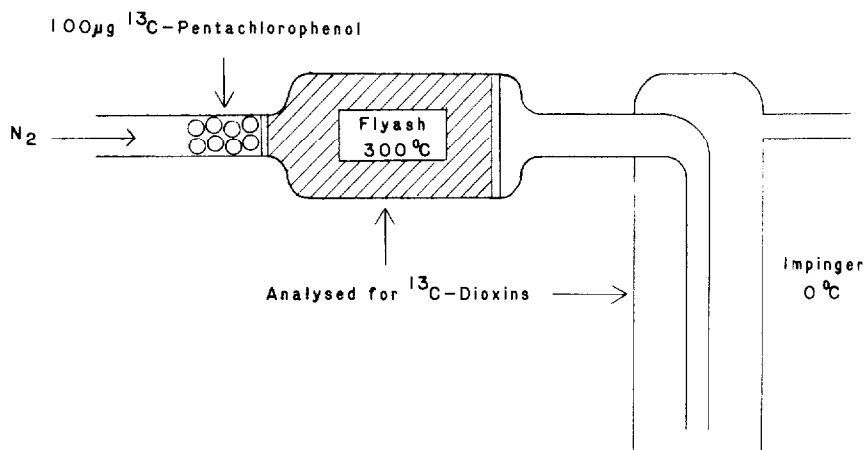


Fig. 1. Schematic of experimental apparatus. Nitrogen flow carries chlorinated phenols to the flyash bed. Reaction products formed on the flyash are extracted from the flyash and the more volatile components are also recovered from the impinger after the experiment.

Ontario was supplied by the Ontario Ministry of the Environment. Machida flyash from a modern fluidized-bed municipal refuse incinerator in Japan was supplied by Dr. H. Hatano (Kyoto University, Kyoto, Japan).

Apparatus and glassware

The apparatus is shown in Fig. 1. All glassware was made of Pyrex.

Glassware was washed in an ultrasonic bath for approximately 30 min using a mild detergent. Following rinsing with deionized water, glassware was dried overnight in an oven at 240°C . Before use glassware was rinsed with solvent. Soxhlet extraction apparatus was rinsed by refluxing benzene for 2 h. The rinse benzene was discarded and fresh benzene used for the flyash extraction. This procedure has been shown effective in removing background impurities from laboratory glassware.

Experimental procedure

About 20 g of exhaustively extracted flyash was placed in the reservoir. This flyash had been heated overnight in the flow-tube at 340°C under a 150-ml/min flow of nitrogen to remove any residual organic material. A bed of glass beads about 35 mm in depth was placed in a section of Pyrex tube which had a coarse glass frit in one end. The glass beads were retained with a plug of glass wool. A volume of $100 \mu\text{l}$ of a 1 mg/ml chlorinated phenol solution in methanol was deposited onto the glass beads and the solvent allowed to evaporate. The tube was fitted to the reservoir with the frit and glass beads just upstream of the flyash. Attached to the other end of the reservoir was a long-armed impinger of 200-ml capacity. This impinger is similar in design to the one used in the Ames Vapour Sampling System¹⁸. The apparatus was placed in a modified gas chromatographic (GC) oven. The impinger resided outside the oven and was cooled with a saturated salt-water-ice bath. A guard trap containing Florisil was attached to the outlet of the impinger. The oven was heated to 300°C over 20 min then a 10-ml/min flow of high-purity nitrogen was passed through

the flow-tube for 1 h maintaining the 300°C temperature throughout. After the experiment was complete the nitrogen flow was stopped and the oven quickly cooled to room temperature. The impinger was removed and the ends sealed with aluminium foil. After rinsing the outside surface of the reservoir with solvent, it was placed in a Soxhlet extractor and the organic compounds extracted with 300 ml benzene for 18 h. The inside surfaces of the impinger were rinsed with 75 ml of dichloromethane, which was transferred to a 300 ml round-bottom flask. The extracts were reduced to several ml by rotary evaporation under reduced pressure. In the event that particulate matter was suspended in the extract after rotary evaporation, the extract was transferred to a centrifuge tube and centrifuged to drive the particles to the bottom. The extract was transferred to a pear-shaped flask and concentrated further. Final concentration to 100 μ l was achieved by flowing a gentle stream of high purity nitrogen over the surface of the sample in a calibrated 1-ml reactival.

Gas chromatographic analysis

To screen the flyash extracts and impinger rinses for chlorinated reaction products samples were analysed on a Hewlett-Packard HP-5880 gas chromatograph equipped with electron-capture detection (ECD) and a cool on-column injector. A 30 m \times 0.32 mm I.D. DB-5 fused-silica capillary column (J & W Scientific, Rancho Cordova, CA, U.S.A.) was used.

Gas chromatographic-mass spectrometric (GC-MS) analysis

Analyses were carried out on a Hewlett-Packard 5987A gas chromatograph-mass spectrometer with an HP1000 data system. The instrument was equipped with a cool on-column injector, a fused-silica 30 m \times 0.32 mm I.D. DB-5 column and a direct inlet GC-MS interface. Instrument operating parameters are given in Table I. Quantitation of chlorinated dioxins was carried out in electron-impact selected-ion

TABLE I
SELECTED ION MONITORING MASS SPECTROMETRY

Chromatographic conditions: fused-silica WCOT column 30 m \times 0.32 mm I.D.; stationary phase, DB-5, 0.25- μ m thickness; helium carrier gas flow, 2.5 ml/min. Temperature programs: GC-ECD: 80°C for 1 min, to 300°C at 3°C/min, hold for 5 min. GC-MS-EISIM: 80°C for 1 min, to 220°C at 20°C/min, to 300°C at 2°C/min, hold for 5 min.

Ions	<i>m/z</i>	Dwell time (ms)
Tetrachlorodibenzo- <i>p</i> -dioxin	319.9, 321.9, 323.9	100
[¹³ C ₁₂]Tetrachlorodibenzo- <i>p</i> -dioxin	267.9, 331.9, 333.9	100
Pentachlorodibenzo- <i>p</i> -dioxin	353.9, 355.9, 357.9	100
[¹³ C ₁₂]Pentachlorodibenzo- <i>p</i> -dioxin	301.9, 365.9, 367.9	100
Hexachlorodibenzo- <i>p</i> -dioxin	387.9, 389.9, 391.9	100
[¹³ C ₁₂]Hexachlorodibenzo- <i>p</i> -dioxin	335.9, 399.9, 401.9	100
Heptachlorodibenzo- <i>p</i> -dioxin	421.8, 423.8, 425.8	100
[¹³ C ₁₂]Heptachlorodibenzo- <i>p</i> -dioxin	369.8, 433.8, 435.8	100
Octachlorodibenzo- <i>p</i> -dioxin	455.7, 457.7, 459.7	100
[¹³ C ₁₂]Octachlorodibenzo- <i>p</i> -dioxin	405.7, 469.7, 471.7	100

monitoring (EISIM) mode. Three isotope ions (M , $M+2$, $M+4$ or $M+2$, $M+4$, $M+6$) were monitored for tetra- to octachloro-*p*-dioxins.

The standard mixture used for external standard quantitation of dioxins contained one isomer each of tetra, penta, hexa, hepta and octachlorodibenzo-*p*-dioxins. Identification of compounds was confirmed using the following criteria:

(1) The mass chromatographic peaks must fall within a retention time window established for a specific class of isomers.

(2) The mass chromatographic peaks produced by the component must exhibit the correct ratios of intensities of ions being monitored.

(3) The signal-to-noise ratio must be greater than 3.

The retention time windows were determined by using mixtures of available isomeric compounds.

RESULTS AND DISCUSSION

^{13}C -labelled pentachlorophenol was passed through a flow-tube containing either Ontario flyash or Machida flyash at 300°C using a flow of 10-ml/min nitrogen

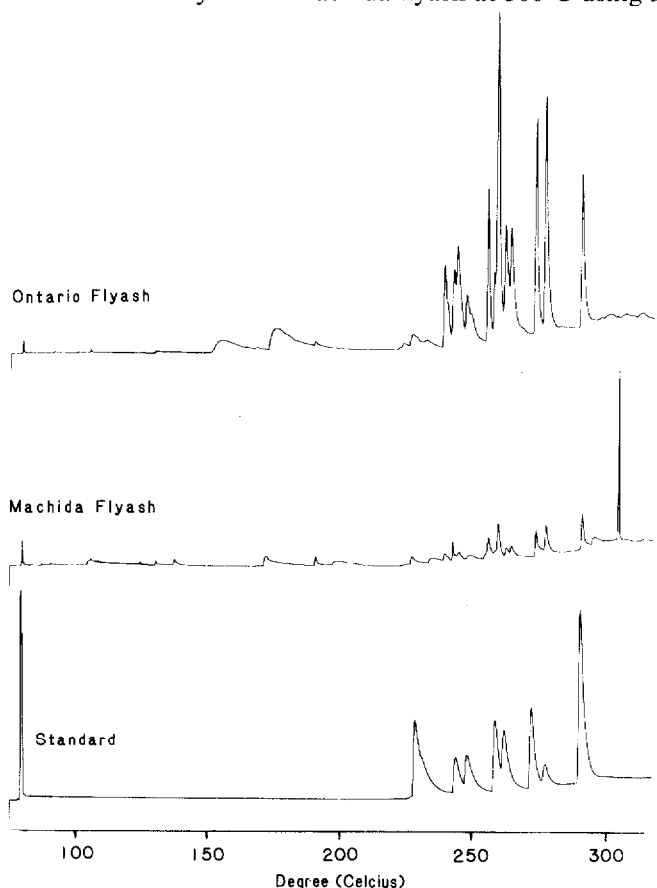


Fig. 2. GC-ECD chromatograms of flyash extracts showing reaction products produced on Ontario and Machida flyash from ^{13}C -labelled pentachlorophenol. The peaks for a standard mixture of tetra- through octachlorodioxins and furans are shown for reference.

gas maintained for 1 h. The GC-ECD analyses of the flyash extracts are shown in Fig. 2. The top chromatogram is an analysis of the extract of the Ontario flyash, the second an analysis of the extract of the Machida flyash. The bottom plot is an analysis of a standard solution containing tetrachloro- to octachlorodioxins and furans at an average concentration of 2 ng/ μ l. The peaks in the chromatograms represent reaction products or the unreacted labelled phenol. Compounds eluting below 200°C are mostly chlorinated benzenes and chlorinated phenols. The compounds eluting above this temperature are the result of the condensation of the chlorinated phenol and other molecular reactions which followed. The experiment using the Ontario flyash yielded much larger amounts of some reaction products than that using Machida flyash. These reaction products elute in the retention time windows characteristic of chlorinated dioxins and furans.

The chromatograms from the EISIM analyses of the reaction products from the experiment using Ontario flyash are shown in Fig. 3. Each plot shows the abundance of the most abundant ion from the molecular ion isotope cluster of the indicated $^{13}\text{C}_{12}$ -labelled chlorinated dibenzo-*p*-dioxin plotted *versus* retention time. The use of a labelled precursor eliminates interferences from possible unextracted compounds on the flyash. It is clear that chlorinated dioxins were formed *in-situ* on the surface of the flyash from the pentachlorophenol precursor. Octachlorodibenzo-*p*-dioxin is likely formed first by the condensation of two phenol molecules. The other chlorinated dioxins arise through the dechlorination of the higher chlorinated species.

The chlorinated dioxins appearing in the impinger rinsings are mainly the tetra- and pentachlorinated isomers. These more volatile compounds are desorbed

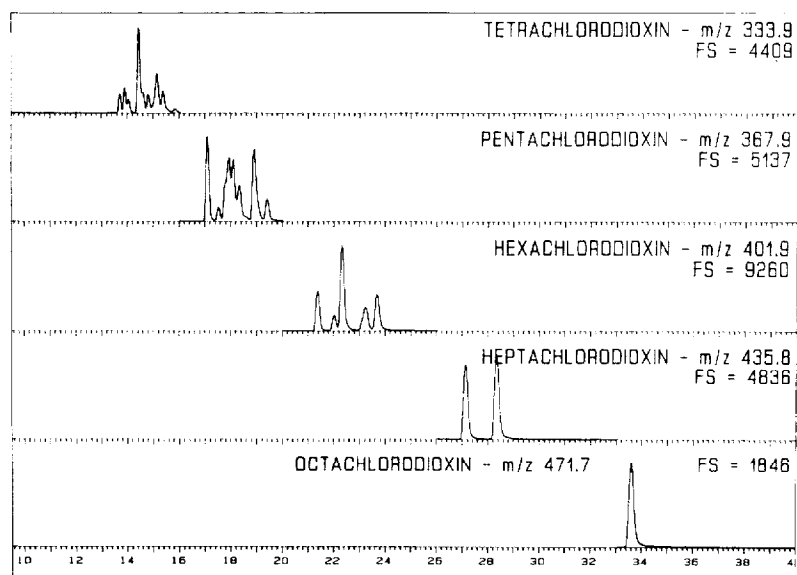


Fig. 3. EISIM data from a GC-MS analysis show $^{13}\text{C}_{12}$ -chlorinated dioxins produced from ^{13}C -labelled pentachlorophenol using Ontario flyash. Each plot shows the abundance of the base peak of the dioxin congener *versus* retention time. The ion mass (m/z) and the plot full scale (FS) values are indicated at the right of each plot.

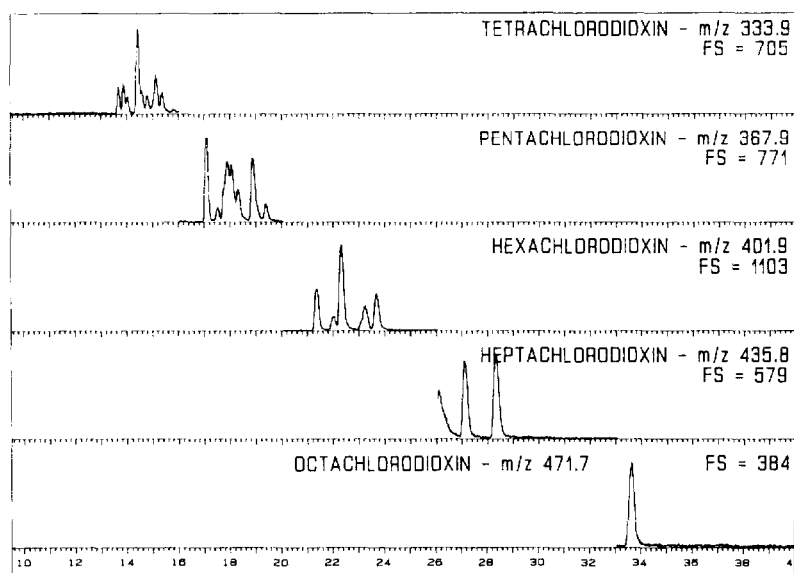


Fig. 4. EISIM data from a GC-MS analysis show $^{13}\text{C}_{12}$ -chlorinated dioxins produced from ^{13}C -labelled pentachlorophenol using Machida flyash. Each plot shows the abundance of the base peak of the dioxin congener versus retention time. The ion mass and the plot full scale values are indicated at the right of each plot.

from the flyash and are carried downstream by the nitrogen flow to condense in the cooled impingers. It has been recently demonstrated that chlorinated dioxins will desorb from flyash surfaces under similar conditions of temperature and flow¹⁹.

The results of the EISIM analyses of the reaction products from the experiment using Machida flyash is shown in Fig. 4. The chlorinated dioxin elution pattern in the flyash extract is remarkably similar to that of the Ontario flyash. The partial peak in the plot of m/z 435.8, heptachlorodioxin, is an impurity, likely a phthalate ester.

The amounts of chlorinated dioxins formed from labelled pentachlorophenol are shown in Fig. 5. The experiment using Ontario flyash produced almost ten times as much chlorinated dioxins as the Machida flyash. It would appear that the latter flyash has a lower catalytic activity than the Ontario flyash. This could be due to differences in the composition of the incinerator fuel feeds or differences in the design and operating conditions of the incinerators.

Both Ontario and Machida flyashes provide a large surface area on which reactions could take place. To determine whether a large surface area is sufficient to produce the large number of isomers observed from reactions of pentachlorophenol, the precursor was passed through a bed of ground firebrick and also through an empty flow-tube. The total amounts of chlorinated dioxins formed using flyash, firebrick and the empty flow-tube are presented in Fig. 6 for comparison. The experiment with the Ontario flyash produced the full range of isomers in the tetra- through octachlorodibenzo-*p*-dioxins similar to those seen in Fig. 3. Octachlorodibenzo-*p*-dioxin and heptachlorodibenzo-*p*-dioxins constitute over 75% of the 3200 ng of chlorinated dioxins produced on the flyash. Approximately 40 ng, 100 ng and 400 ng of

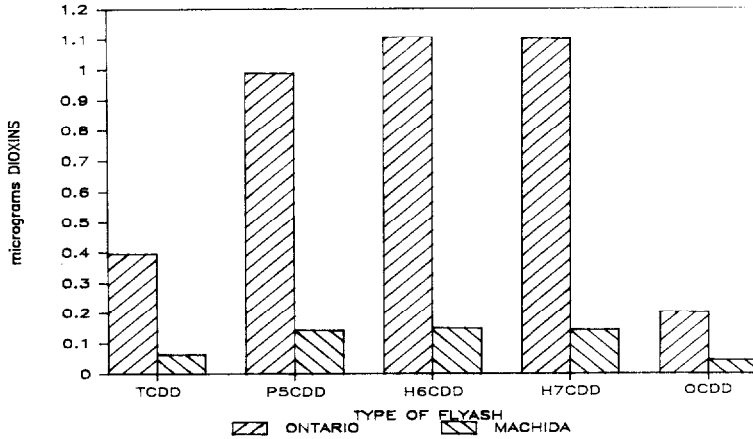


Fig. 5. Bar chart showing the amounts of $^{13}\text{C}_{12}$ -chlorinated dioxins formed from 100 μg of ^{13}C -labelled pentachlorophenol using Ontario and Machida flyash. Over 3.2 μg of chlorinated dioxins were formed from 100 μg of pentachlorophenol using Ontario flyash. Abbreviations: TCDD = tetrachlorodibenzo-*p*-dioxin; P5CDD = pentachlorodibenzo-*p*-dioxin; H6CDD = hexachlorodibenzo-*p*-dioxin; H7CDD = heptachlorodibenzo-*p*-dioxin; OCDD = octachlorodibenzo-*p*-dioxin.

tetra-, penta- and hexachlorodibenzo-*p*-dioxins were produced, respectively. A significant amount of octachlorodibenzo-*p*-dioxin was produced using the empty flow-tube, whereas the firebrick alone produced almost immeasurable amounts. Since the octachlorodibenzo-*p*-dioxin produced using firebrick and an empty flow-tube correspond to that produced purely by thermal reaction of the pentachlorophenol, clearly the catalytic constituents of the flyash promote not only the formation of large amounts of octachlorodibenzo-*p*-dioxin but also large amounts of all the lower chlorinated dioxins. The total amount of chlorinated dioxins produced on flyash was ten times the amount produced by the experiment using an empty flow-tube. It was expected that the firebrick and empty flow-tube experiments would have produced

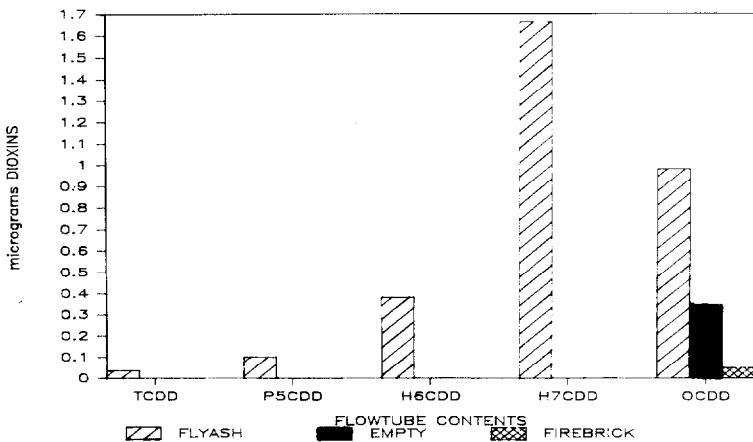


Fig. 6. Bar chart comparing the amounts of chlorinated dioxin reaction products formed from 100 μg of pentachlorophenol using Ontario flyash, firebrick or an empty flow-tube. Abbreviations as in Fig. 5.

similar amounts of octachlorodioxin. The difference, we speculate, may be due to the firebrick inhibiting the condensation of the chlorinated phenol to octachlorodioxin.

It is clear that surface area is not a factor in producing large numbers of dioxin isomers from pentachlorophenol. The ground firebrick has a specific surface area of $3.8 \text{ m}^2/\text{g}$, which is comparable to the Ontario flyash specific surface area of $3.2 \text{ m}^2/\text{g}$ and the Machida flyash specific surface area of $2.2 \text{ m}^2/\text{g}$. These surface areas are orders of magnitude smaller than those of heterogeneous catalysts. These results indicate that the flyash surface has constituents and properties that promote the production of chlorinated dioxins from pentachlorophenol.

Having established that Ontario flyash will catalyse the production of chlorinated dioxins from pentachlorophenol, the experiments were repeated using 2,4,5-trichlorophenol and 3,4,5-trichlorophenol. The results of these experiments are shown in Fig. 7. These chromatograms are made from EISIM analyses of the total reaction products. The distributions of the dioxin isomer from these chromatograms are clearly very different. The experiments using 2,4,5-trichlorophenol produced mainly hexachlorodibenzo-*p*-dioxins and very little of the tetra- and octachlorinated isomers. Also, within each congener group there are several peaks whose relative abundances are greater than those found in the experiments using pentachlorophenol or in the analyses of chlorinated dioxins extracted from the Ontario flyash before treatment. This would indicate that there are certain isomers whose production is favoured over the others, implying that certain positions on the benzene rings are more reactive to chlorination or dechlorination than the others.

The experiment using 3,4,5-trichlorophenol yielded very interesting results, in that dioxins were formed at all from a chlorinated phenol that did not possess a chlorine atom *ortho* to the hydroxyl group. Condensation and ring closure to form dioxins from chlorinated phenols requires *ortho*-substitution. Some scrambling of the

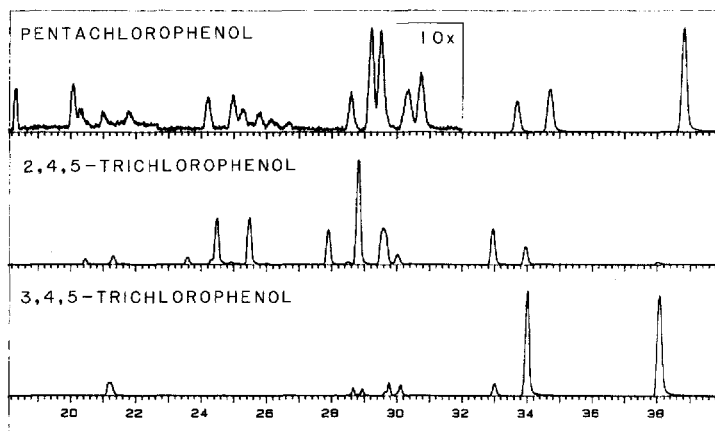


Fig. 7. EISIM data from GC-MS analyses of the chlorinated dioxin reaction products formed on Ontario flyash using three different chlorinated phenols are plotted *versus* retention time. Each plot is labelled with the chlorinated phenol used in the experiment. The dioxin isomer distributions appear to be dependent upon the chlorine substitution pattern of the reactant. The retention time window for tetrachlorodioxins is 19–23 min; for pentachlorodioxins, 23–27 min; hexachlorodioxins, 27–32 min; heptachlorodioxins, 32–35 min; octachlorodioxin, 35–39 min.

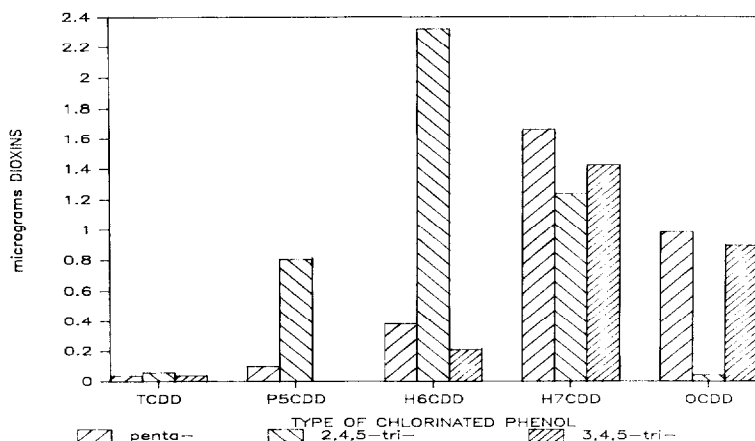


Fig. 8. Bar chart comparing the amounts of chlorinated dioxin reaction products formed on Ontario flyash using the three different chlorinated phenols shown in Fig. 7. Abbreviations as in Fig. 5.

chlorine and hydroxyl group positions must take place for dioxins to be formed from this precursor. The dioxin isomer distribution is very different from the distributions arising from 2,4,5-trichloro- and pentachlorophenol. The major peaks are octachlorodibenzo-*p*-dioxin and 1,2,3,4,5,6,7,8-heptachlorodibenzo-*p*-dioxin. The relatively small amount of the other heptachloro isomer suggests that the 9-position on the dioxin molecule is less easily chlorinated than the 8-position. The lesser chlorinated isomers were present only at very low levels, with pentachlorodibenzo-*p*-dioxin detected at the detection limit of 100 pg/ μ l (100 μ l total sample volume).

The total amounts of each dioxin congener group produced in the experiments using penta-, 2,4,5-tri- and 3,4,5-trichlorophenol are shown in Fig. 8. The major reaction products from the 2,4,5-trichlorophenol isomer are hexa- and heptachlorodibenzo-*p*-dioxins. Considering that chlorination and dechlorination are competing processes, it would be expected that these dioxins possessing a degree of chlorination midway between the tetrachlorodibenzo-*p*-dioxins (the condensation product) and octachlorodibenzo-*p*-dioxin would predominate. The large amount of the octachlorinated and heptachlorinated isomers produced using 3,4,5-trichlorophenol and the lack of any significant amounts of pentachlorodibenzo-*p*-dioxin would indicate a different route to the dioxins than that taken by the other chlorinated phenols possessing an *ortho*-substituted chlorine. The phenol may undergo rearrangement or isomerization due to dechlorination, dehydrogenation, *trans*-chlorination and other similar molecular reactions before condensation to form a chlorinated dioxin. The various competing reactions and the reactivity of the intermediates would be reflected in the amounts and kinds of isomers formed.

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