Reports

Model Studies of Polychlorinated Dibenzo-*p*-Dioxin Formation During Municipal Refuse Incineration

F. W. Karasek and L. C. Dickson

Toxic chlorinated dibenzo-*p*-dioxins are known to be formed in incinerators that burn municipal refuse. These compounds were synthesized by surface-catalyzed reactions on fly ash particulates taken from incinerators. Dioxins were produced catalytically from chlorinated phenol precursors, from non-chlorinated compounds that were chemically dissimilar to dioxins, and from reaction of phenol with inorganic chlorides. The relative amounts of dioxins formed from [$^{13}C_6$]pentachlorophenol with different fly ashes that had been cleaned of all organic compounds corresponded well with those amounts originally found on the samples as received from the incinerators. The optimum temperature range for the formation of dioxins from pentachlorophenol was 250° to 350°C.

The inorganic constituents of refuse in the combustion zone of a municipal incinerator form fine particulate matter called fly ash that becomes entrained in the combustion gases that are exhausted to a stack. More than 600 organic compounds adsorbed on the fly ash have been identified. Polychlorinated dibenzo-*p*-dioxins (commonly referred to as dioxins) were first detected in the precipitated fly ash from a municipal refuse incinerator by Olie and Hutzinger in 1977 (*1*). Since then numerous studies have established that dioxins are formed during refuse incineration (*2*). The presence of dioxins in the effluent of incinerators is important since some dioxin isomers, especially 2,3,7,8-tetrachlorodioxin, have shown high toxicity and carcinogenic effect in animal studies (*3*). Public concern about dioxins has impeded the construction and use of new incineration facilities (*4*).

The mechanism of dioxin formation during incineration is not understood. Bumb noted that chlorinated polynuclear aromatic compounds such as dioxins, dibenzofurans, and polychlorinated biphenyls could be formed either from reactions of compounds at low concentrations or formed as a result of low-yield reactions of more concentrated compounds (*5*). Lustenhouwer, Olie, and Hutzinger presented three possible mechanisms: (i) survival of trace levels of dioxins in the fuel, (ii) generation from precursors such as chlorinated phenols, and (iii) thermal synthesis from unrelated material and inorganic chlorine (*6*). Shaub and Tsang developed thermodynamic and kinetic models in favor of heterogeneous gas–solid phase reactions (*7*). Eiceman and Rghei showed that gas–solid phase chlorination of dioxins adsorbed onto fly ash by gaseous hydrogen chloride is rapid and efficient (*8*). We present evidence that dioxins can be produced from known precursors and other chemically dissimilar compounds by surface-catalyzed reactions on fly ash particulates under mild conditions.

Precipitated fly ash was taken from: (i) a refractory-wall municipal refuse incinerator in Toronto, Canada; (ii) a modern fluidized-bed municipal refuse incinerator in Machida, Japan, and (iii) the effluent stream of a copper-refinery reactor in Noranda, Canada, that used ground copper wire that was insulated with polyvinyl chloride (PVC) as supplemental fuel. Chromosorb P non-acid-washed chromatographic support (Johns-Manville) derived from crushed firebrick was also used as a control. Aliquots of the fly ash and firebrick (40 g) were extracted with benzene before use to remove adsorbed organic material. The fly ash and firebrick were heated in separate experiments in a borosilicate glass apparatus with the reactants while maintaining a flow of high-purity nitrogen through the apparatus; the products were then extracted and concentrated (*9*). The products were analyzed for dioxins by high-resolution gas chromatography–low-resolution mass spectrometry (GC-MS). Qualitative and quantitative analyses were performed with electron impact selected ion monitoring (EISIM) of the parent ion isotope cluster $[M + 2]^+$, $[M]^+$, and $[M{-}COCl]^+$ ions for tetrachloro- through heptachlorodioxins and the $[M + 4]^+$, $[M + 2]^+$, and $[M{-}COCl]^+$ ions for octachlorodioxin (where M is the parent molecule). The external standard used contained one isomer each of tetra-, penta-, hexa-, hepta-, and octachlorodioxins that had a 2,3,7,8-chlorine substitution pattern.

The ability of different particulate materials to catalyze the formation of dioxins was probed by using [$^{13}C_6$]pentachlorophenol. The labeled pentachlorophenol was passed through the reservoir of the apparatus that contained either one of the fly ashes or ground firebrick at 300°C and in which a flow of 10 ml/min of nitrogen was maintained for 1 hour. The ground firebrick was used to test whether a large surface area alone was sufficient for the formation of all the dioxin isomers observed from pentachlorophenol and also as a control for the large amounts of firebrick that are present in municipal incinerators. The amounts of each dioxin congener (isomers that contain the same number of chlorines) produced with the different substrates are presented in Table 1.

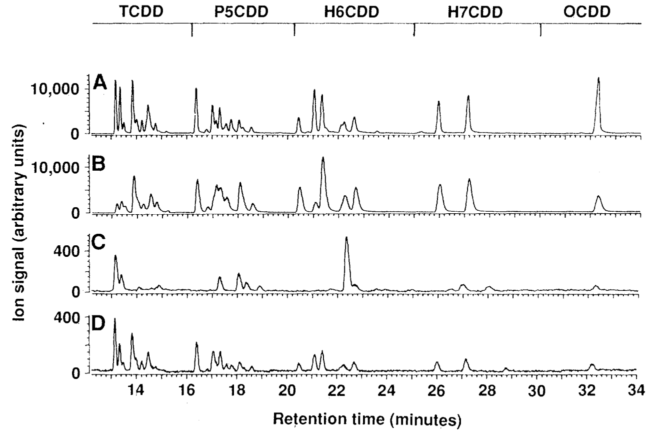
The experiment with Ontario fly ash pro-

Table 1. Amounts of dioxins produced with Ontario fly ash in a municipal incinerator (per gram of fly ash) and in the laboratory on different fly ashes from 100 μg of [$^{13}C_6$]pentachlorophenol. A blank entry indicates that less than 4 ng of dioxin was formed. The average deviations given for original Ontario fly ash are based on duplicate analyses. These deviations represent the analytical error. The average deviations are based on duplicate experiments with Ontario fly ash and labeled pentachlorophenol. The relative deviations, which range from 11 to 53%, are typical of values obtained from similar experiments in our laboratory. Entries for Machida and Noranda fly ashes are based upon single experiments. Abbreviations: tetrachlorodioxin, TCDD; pentachlorodioxin, P5CDD; hexachlorodioxin, H6CDD; heptachlorodioxin, H7CDD; octachlorodioxin, OCDD.

Matrix	Amount of dioxin congeners (ng)				
	TCDD	P5CDD	H6CDD	H7CDD	OCDD
Original Ontario fly ash	521 ± 70	1433 ± 144	1676 ± 175	1774 ± 117	469 ± 25
Ontario fly ash	218 ± 117	571 ± 225	1041 ± 119	1559 ± 486	430 ± 221
Machida fly ash	54	115	121	132	40
Noranda fly ash				11	18
Ground firebrick					4
Empty reservoir					267

Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

Fig. 1. EISIM chromatograms of dioxins produced on Ontario fly ash: (**A**) in a municipal incinerator and in the laboratory apparatus from (**B**) [$^{13}C_6$]pentachlorophenol; (**C**) a mixture of selected PVC pyrolysis products and (**D**) a mixture of PVC combustion products. Each plot shows the signal for the most abundant ion as a function of retention time. Abbreviations are as in Table 1.



duced about seven times the amount of dioxins as the experiment with Machida fly ash. Only trace amounts of heptachlorodioxins and octachlorodioxin were detected in the reaction products from the experiment with Noranda fly ash. The relative amounts of dioxins produced in our experiments with these fly ashes correspond well with those originally found on the samples as received from the incinerators. Only octachlorodioxin, which would be the product of thermal condensation of two pentachlorophenol molecules, was detected in the experiments with firebrick or an empty reservoir. The dioxins observed with the Ontario and Machida fly ashes were formed on their surfaces from the labeled pentachlorophenol precursor (*10*). Octachlorodioxin is probably formed first by the condensation of two pentachlorophenol molecules; the other dioxins are then produced through dechlorination of the more highly chlorinated isomers.

[$^{13}C_6$]Pentachlorophenol was passed through Ontario fly ash at different temperatures (Table 2). The maximum yield of dioxins, 4.1%, was observed at 250°C; the octachloro- and heptachlorodioxins predominated. A temperature increase of only 50°C caused large amounts of tetrachloro-, pentachloro-, and hexachlorodioxins to form.

All of the fly ash and firebrick samples used had similar physical characteristics such as specific surface area (2.3 to 3.6 m^2/g) and average pore diameters (760 to 1450 nm). The specific surface areas were orders of magnitude less than those of heterogeneous catalysts. The results indicate that the Ontario fly ash, and to a lesser extent the Machida fly ash, promoted the production of chlorinated dioxins from pentachlorophenol.

Chlorinated dioxins were also produced from 2,4,5-trichlorophenol and 3,4,5-trichlorophenol precursors. The dioxin isomer distributions were different from that produced from pentachlorophenol. The experiment with 2,4,5-trichlorophenol produced primarily hexachlorodioxins, whereas octachlorodioxin and heptachlorodioxin were the major products of the experiment with 3,4,5-trichlorophenol.

Table 2. Amounts of [$^{13}C_{12}$]dioxins produced at different temperatures from 100 μg of [$^{13}C_6$]-pentachlorophenol with Ontario fly ash as the catalyst. A blank entry indicates that less than 4 ng of dioxin was formed; the + symbol indicates that dioxin was detected but could not be quantified. Entries for 300°C are based on duplicate experiments. Other entries are based on single experiments. Abbreviations are as in Table 1.

Temperature (°C)	Amount of dioxin congeners (ng)				
	TCDD	P5CDD	H6CDD	H7CDD	OCDD
150					+
250			29	583	3463
300	218	571	1041	1559	430
340	61	228	392	384	50
400	8	17	34	70	14

Table 3. Amounts of dioxins produced with Ontario fly ash in a municipal incinerator (per gram fly ash) and in the laboratory apparatus from a mixture of selected PVC pyrolysis products (cinnamyl chloride, 2-chloro-*p*-xylene, and naphthalene, 100 μg of each compound) and for a mixture of PVC combustion products. The deviations are based on duplicate analyses of Ontario fly ash; these deviations represent the analytical error. Entries for selected PVC compounds and PVC combustion products are based on single analyses. Abbreviations are as in Table 1.

Mixture	Amount of dioxin congeners (ng)				
	TCDD	P5CDD	H6CDD	H7CDD	OCDD
Original Ontario fly ash	521 ± 70	1433 ± 144	1676 ± 175	1774 ± 117	469 ± 25
Selected PVC compounds	63	113	161	116	41
PVC combustion products	25	33	30	24	5

An analysis for surface elements of the fly ashes and firebrick with x-ray photoelectron spectroscopy (XPS) showed that chlorine is present along with the metallic elements on the Ontario and Machida fly ash but not on the Noranda fly ash and the ground firebrick. The pentachlorophenol experiments were repeated with [$^{13}C_6$]phenol to determine if inorganic chlorides on the fly ash surface would both chlorinate the aromatic ring and promote the formation of dioxins. Phenol did react with the Ontario fly ash surface; 400 μg of [$^{13}C_6$]phenol reacted to form 234 ng of tetrachlorodioxin, 63 ng of pentachlorodioxin, and 7 ng of hexachlorodioxin. No heptachlorodioxins or octachlorodioxins were detected. Significant levels of monochloro-, dichloro-, and trichlorodioxins may have been produced but these compounds were not determined. The low yield of dioxins from phenol (~0.1%) indicates that chlorination of the phenol ring by inorganic chlorides is not especially favored under these conditions. These data provide evidence that inorganic chlorides on the Ontario fly ash surface are involved in the reaction mechanism.

The mechanism of the catalyzed formation of the dioxins could encompass some aspects of the theory postulated by Shaub and Tsang. A chemisorbed precursor molecule could become very reactive due to the removal of hydrogen or chlorine atoms from the bound molecule by neighboring reactive sites on the fly ash.

We also studied the reactivity of the combustion products of PVC. Two experiments were performed. A mixture that contained three compounds, which were identified as pyrolysis products of PVC (cinnamyl chloride, 2-chloro-*p*-xylene, and naphthalene), was prepared with a concentration of 1 g/liter of each component (*11*). Also, a sample of commercial grade PVC that contained plasticizers, binders, and carbon black pigment was heated to 600°C in a quartz tube and combusted in an air stream. The combustion products were collected, concentrated, and deposited on glass beads. Experiments were then conducted as previously described for the pure compounds with Ontario fly ash as the catalyst. In Fig. 1 a comparison is made of EISIM chromatograms of dioxins extracted from Ontario fly ash collected from a municipal incinerator and dioxins formed in the laboratory apparatus from [$^{13}C_6$]pentachlorophenol, from a mixture of selected PVC pyrolysis products, and from a mixture of PVC combustion products (Table 3). The chromatograms show the similarity in the isomer distributions of dioxins formed from labeled pentachlorophenol and from PVC combustion products with that of dioxins extracted from fly ash collected from the municipal incinerator.

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9. About 20 g of the fly ash was placed in a borosilicate glass reservoir of 35-ml capacity which had a coarse glass frit at one end. A bed of glass beads 35 mm deep was placed in a section of borosilicate glass tube that also had a coarse glass frit at the end. A 100-μl methanol solution that contained either a single pure compound or a mixture of compounds at a concentration of about 1 g/liter was deposited onto the glass beads just upstream of the fly ash. Attached to the other end of the reservoir was a long-armed impinger of 200-ml capacity. The reservoir and glass beads were heated to the reaction temperature; high-purity nitrogen was then passed through the connected tube and reservoir. Organic compounds formed in the experiment that either desorbed from the fly ash or passed through unreacted were collected in the impinger held at −10°C. At the end of the experiment the organic compounds on the fly ash were extracted by placing the reservoir with the fly ash in a soxhlet extractor and refluxing with 300 ml of benzene for 18 hours. The inside surfaces of the impinger were rinsed with dichloromethane. The extracts were concentrated by evaporation to a final volume of 100 μl. Fly ash and impinger extracts were analyzed separately.
10. Pentachlorophenol melts at 180°C and vaporizes at 340°C [H. P. Langer, T. P. Brady, L. A. Dalton, T. W. Shannon, P. R. Briggs, in *Chlorodioxins—Origin and Fate*, vol. 120 of *Advances in Chemistry Series* (American Chemical Society, Washington, DC, 1973), p. 26]. At 150°C the vapor pressure would be very low. The low yield of dioxins could be due to the small amount of pentachlorophenol that was transferred to the fly ash; thus 100 μg of pentachlorophenol was deposited directly to the fly ash in the reservoir and the experiment at 150°C was repeated. Almost 250 ng of octachlorodioxin was produced, which was a 125-fold increase over the amount in the previous experiment at 150°C. Also, the amount is comparable to the amount of octachlorodioxin formed at 300°C in the absence of fly ash. The fly ash seems to promote the condensation of two phenol molecules into a dioxin molecule in addition to catalyzing chlorination and dechlorination reactions.
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12. We thank the Natural Sciences and Engineering Research Council, Canada, and the Ontario Ministry of the Environment for financial support. We also thank M. O'Mara of the Vinyl Institute for characterizing the particulate samples.

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Disulfate Ion as an Intermediate to Sulfuric Acid in Acid Rain Formation

S. G. Chang, D. Littlejohn, K. Y. Hu*

The oxidation of the bisulfite ion by dissolved oxygen to produce sulfate ion involves the formation of a previously undetected intermediate. This intermediate has a fairly strong Raman band at 1090 wave numbers and a weak Raman band at 740 wave numbers, both of which are probably due to sulfur-oxygen stretches. The intermediate is proposed to be the disulfate ion $S_2O_7^{2-}$, which hydrolyzes into H^+ and either SO_4^{2-} or HSO_4^{2-} with a half-life of about 52 seconds at 25°C.

Sulfur dioxide (SO_2), which is produced from combustion of fossil fuels, can be oxidized to sulfuric acid in the atmosphere and contribute to acid rain formation. Many oxidation pathways can occur in the atmosphere (*1*), one of which is the oxidation of SO_2 by O_2 in aqueous droplets such as in fog, clouds, and rain. This oxidation reaction has been studied for almost a century and yet the oxidation mechanism is unclear. Rate laws and rate constants obtained for this reaction by previous investigators have been inconsistent because the reaction is very sensitive to many kinds of impurities; some of these impurities act as catalysts, while others are inhibitors at very low concentrations. Most of these kinetic studies were performed at atmospheric pressure by measuring the consumption rate of one of the reactants or the production rate of sulfate ion by conventional wet analytical methods. The concentrations of the other species were inferred from the stoichiometry of the reaction

$$2HSO_3^- + O_2 \rightarrow 2SO_4^{2-} + 2H^+ \qquad (1)$$

Unlike the approaches used by previous investigators, we have studied this reaction under high-pressure conditions with laser Raman spectroscopy (LRS) to monitor the dynamics of all known species involved during the course of the reaction. With this approach we have found that a mass balance of sulfur and oxygen cannot be achieved for the entire course of the reaction by just considering the known species. Subsequently, a previously undetected intermediate that is present in substantial quantity and relatively long-lived was discovered.

The high-pressure rapid-mixing flow system used in our study can be pressurized to 100 atm so that a sufficiently high dissolved oxygen concentration can be detected by LRS. In addition to dissolved oxygen, all of the other important species in the reaction system can be observed with LRS: SO_2 (aq), HSO_3^-, SO_3^{2-}, HSO_4^-, SO_4^{2-}, $S_2O_5^{2-}$, and $S_2O_6^{2-}$. Sodium perchlorate was added to the reaction mixture as a reference so that quantitative measurements could be made.

Atmospheric water droplets are often very acidic. The *p*H of water droplets is 5.6 when in equilibrium with 0.03% CO_2 in air. The dissolution of SO_2 and NO_x can further lower this value. Measurements of fog droplets and rain at many locations worldwide have yielded *p*H values less than 4 (*2*). Under acidic conditions HSO_3^- will be the dominant species from the dissolution of SO_2 in aqueous solutions. Thus we performed most of the experiments in our study

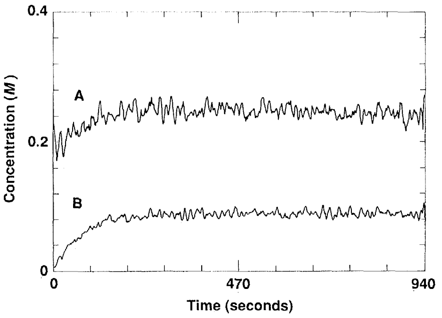

Fig. 1. Mass balance as a function of time (run 57) for (**A**) sulfur-containing and (**B**) oxygen-containing species. In both cases the initial *p*H was 4. The initial sulfur concentration was 0.25*M* in (A), whereas the initial oxygen concentration was 0.08*M* in (B).

Applied Science Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

*On leave from the Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing, People's Republic of China.