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THE ROLE OF GAS-PHASE Cl_2 IN THE FORMATION OF PCDD/PCDF DURING WASTE COMBUSTION

Kevin R. Bruce and Laura O. Beach
Acurex Corporation, Research Triangle Park, North Carolina 27709, U.S.A.

*Brian K. Gullett**
United States Environmental Protection Agency, Air and Energy Engineering Research Laboratory, Research Triangle Park, North Carolina 27711, U.S.A.

ABSTRACT. Results of previous experiments investigating formation of polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/PCDF) through low-temperature (300°C), fly-ash-catalyzed reactions are demonstrated to have occurred through intermediate formation of gas-phase Cl_2 by decomposition of the added catalyst, $CuCl_2$. The dependence of PCDD/PCDF formation rates on Cl_2 concentration is shown and the implications of the Deacon process on these rates discussed. A scheme for controlling the formation of PCDD/PCDF during incineration using sorbent materials to remove the source of Cl at high temperatures is proposed.

INTRODUCTION

The presence of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in the stack gas and on fly ash from both municipal and hazardous waste incinerators is of great concern because of the toxicity of these chemicals. Results of theoretical modeling and experimental work have shown that decomposition of PCDD/PCDF is favored over their formation at temperatures greater than 600°C (1,2). This suggests that PCDD/PCDF found in incinerator fly ash or stack gas result neither from carryover of PCDD/PCDF initially present in the waste feed nor from formation in the high temperature combustion zone. Experimental evidence favors PCDD/PCDF formation mechanisms involving *de novo* synthesis through heterogeneous, fly ash-catalyzed reactions at temperatures around 250–350°C (3, 4, 5). Various copper compounds, particularly those having Cu(II), have been proposed as the likely active catalysts in fly ash (3,6). The chlorinating species in PCDD/PCDF formation has been proposed to be gas-phase Cl_2, but the source of the Cl is in debate. Stieglitz *et al.* (3) propose that metal chlorides present in fly ash give rise to HCl, which is converted to Cl_2 via the Deacon process. The Deacon process utilizes either CuCl or $CuCl_2$ as a catalyst in the presence of O_2 and is effective at temperatures between 300 and 550°C (7). Alternatively, other researchers have suggested that the HCl participating in the Deacon process results from combustion of organic compounds containing Cl (6,8). Gas-phase Cl_2 from the Deacon process was suspected as the Cl source in formation of PCDD/PCDF because test results with other aromatic hydrocarbons have shown that chlorination takes place rapidly in the presence of Cl_2 (9).

Previous experiments performed in quartz tube furnaces by other researchers using both actual and simulated municipal waste combustor fly ash showed that PCDD/PCDF formation occurred readily at 300°C in the presence of O_2 (10). Formation increased when the process gas was doped with HCl or when incinerator stack gas containing HCl was used, suggesting that the Deacon process, converting HCl to Cl_2, played a role. Tests on simulated fly ash, doped with $CuCl_2$ as a source of Cu(II) for catalysis and KCl as a Cl source, likewise showed formation at 300°C in the presence of O_2, even without HCl addition (3). Increasing the amount of $CuCl_2$ increased PCDD/PCDF production, presumably by providing additional catalytic sites. Production in

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*To whom correspondence should be addressed.
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these tests, in the absence of HCl for conversion to Cl_2, would appear to confirm that the Cl came from the KCl added to the simulated fly ash.

In our work, tests in a quartz tube furnace reactor were used to investigate the decomposition of the $CuCl_2$ catalyst under reaction conditions representative of those used in previous studies. Tests were run in the presence of a Cu(II) catalyst with either KCl or gas-phase Cl_2 as the assumed Cl source. Furthermore, the effects of Cl_2 concentration on PCDD/PCDF formation were studied. The purpose of the research was to determine the source of Cl for PCDD/PCDF formation and to assess possible control mechanisms.

EXPERIMENTAL

Tests were run in a quartz tube reactor described in an earlier work (9) and shown in Fig. 1. Except where noted, 1 g of the catalyst of interest was embedded in a quartz wool bed and placed in the center of the inner tube of the reactor, then heated to 300°C. Gases, made up of 10% O_2 in N_2, were set to give approximately 1 L/min flow at 300°C. Low concentrations of Cl_2 (79.1–633.2 mg/Nm^3 or 25–200 ppm), taken from a compressed gas cylinder, were added to some experiments, as was vapor-phase phenol (C_6H_5OH) at a level of approximately 2,100 mg/Nm^3 (500 ppm), added by passing N_2 through a phenol-filled vessel submerged in a heated water bath. Figure 1 shows alternate gas absorption trains for inorganic or organic sampling. The inorganic sampling train, designed for quantifying Cl_2, consists of two impingers filled with a buffered potassium iodide (KI) solution as described in Fisher *et al.* (11). Cl_2 reacts quantitatively with the KI solution to form I_2 which is in turn titrated with a standardized sodium thiosulfate solution using a starch indicator.

In the experiments using phenol, the reactor effluent was bubbled through two ice-cooled impingers filled with toluene (C_7H_8). After 30 min with gas flow through the reactor, the catalyst plug was cooled, removed from the reactor, and placed in an extraction thimble, where it was spiked with $^{13}C_{12}$-labeled internal PCDD and PCDF standards. The reactor and all the lines of the sampling system were rinsed with toluene, the rinsings combined with the liquor from the impingers, and all the liquid added to a soxhlet extractor, where the catalyst plug was extracted overnight. Following this step, the extract was concentrated and solvent-exchanged to hexane (C_6H_{14}). The sample was then extracted in a sepa-

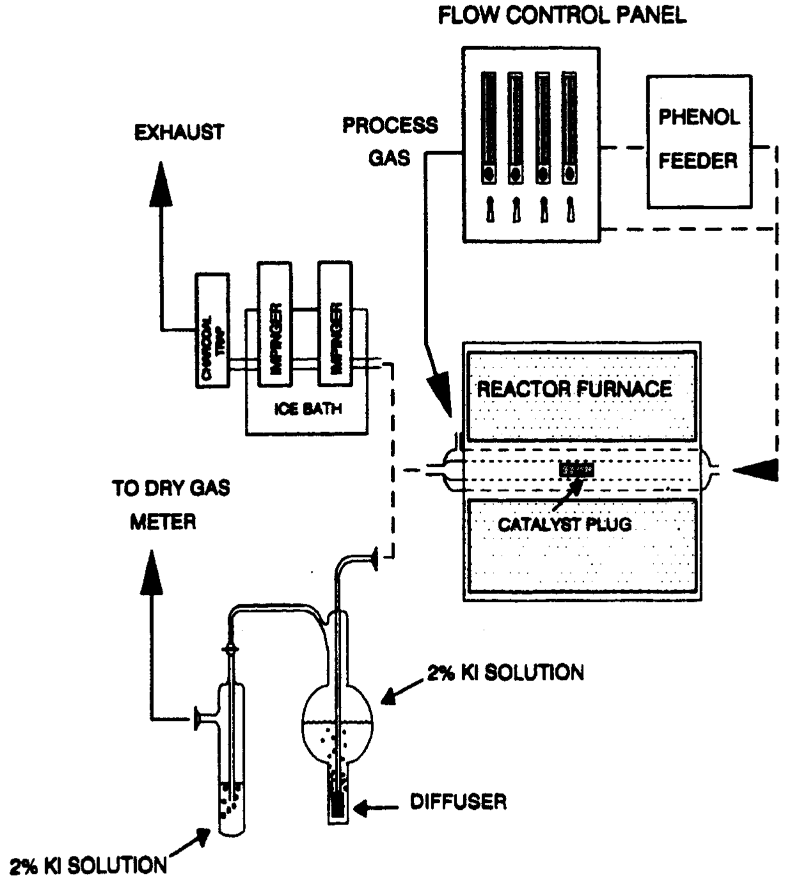

FIGURE 1. Test apparatus.

ratory funnel with 30 mL of 1M KOH and the aqueous layer discarded. The organic phase was then extracted with three 50 mL aliquots of concentrated H_2SO_4, filtered, and dried over Na_2SO_4. The sample was cleaned using, in order, silica, alumina, and carbon columns. The sample was then gently blown down to dryness, spiked with a $^{6}C_{12}$-labeled PCDD recovery standard, and brought to a volume of 100 μL. Injections of 2 μL were run on an HP 5890 GC equipped with an HP 5970 MSD and a 30 m DB5 column from J&W Scientific and were quantified in acceptance with the guidelines in Environmental Protection Agency (EPA) Method 8280 (12).

RESULTS

Because previous experiments (9) had shown that the Deacon process catalyst CuCl decomposed to form Cl_2 at the test conditions used in that work (400 °C), similar decomposition tests were performed on the $CuCl_2$ catalyst used by Stieglitz *et al.* (3). Flowing N_2 alone through a $CuCl_2$ catalyst plug at 300 °C did not produce any measurable Cl_2. Adding 10% O_2 to the process flow however resulted in production of Cl_2 gas as detected by the KI solution and shown in Fig. 2. Increasing the amount of $CuCl_2$ present in the reactor resulted in production of increased amounts of Cl_2. This would indicate that Cl_2 gas, from decomposition of the $CuCl_2$, was present during the experiments described by Stieglitz. Addition of several alkali metal chlorides including KCl, $CaCl_2$, and NaCl to the $CuCl_2$ plug had no effect on the Cl_2 emission rate.

To determine which of the sources of elemental Cl present in the Stieglitz *et al.* (3) experiments contributed to the formation of PCDD/PCDF, KCl (as suggested in the referenced paper) or Cl_2 gas evolved from the $CuCl_2$ catalyst, a series of experiments with phenol as a source of carbon (C) was performed. A blank test with quartz wool only was run initially to identify background levels of PCDD/PCDF present as contaminants in the solvents and glassware used. A test with 1 g KCl as the Cl source and 1 g CuO as the Cu(II) catalyst was run next. Additional catalyst combinations tested were 1 g $CuCl_2$ only and a mix of 1 g $CuCl_2$ with 1 g KCl. Figure 3 (a and b) shows the results for PCDD/PCDF production in these experiments. Only trace levels were found for the blank (QW only) and for the CuO/KCl runs. For the runs with $CuCl_2$ however, elevated amounts of PCDD and PCDF were found. No enhancement of production can be noted for the $CuCl_2$/KCl sample over the sample with $CuCl_2$ alone.

To measure the effect of Cl_2 concentration on formation of PCDD/PCDF, experiments were run using 1 g CuO as the Cu(II) catalyst and doping various amounts of Cl_2 into the process stream. Tests were run at concentration levels of 79.1, 158.3, 316.6, and 633.2 mg/Nm^3 (25, 50, 100, and 200 ppm). Results from these tests are shown in Fig. 4 (a and b). It is clear from the data that increasing Cl_2 concentration results in increased formation of PCDD/PCDF. Replication of selected tests confirmed the noted trend.

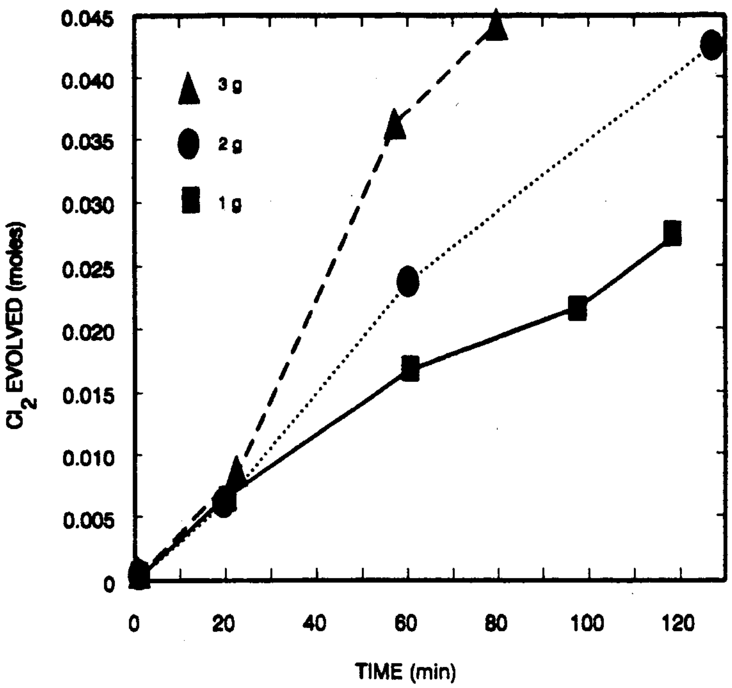

FIGURE 2. Decomposition of $CuCl_2$ catalyst.

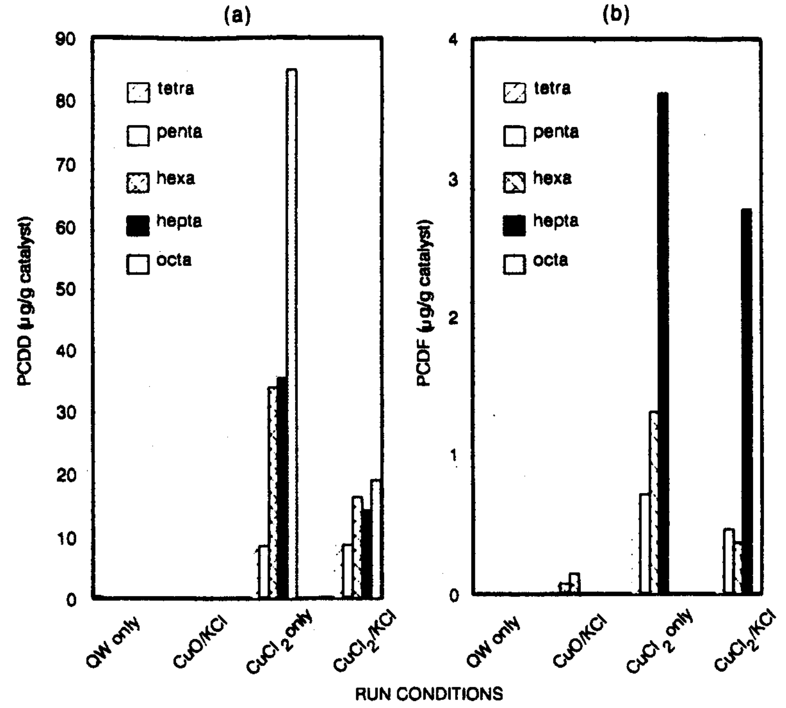

FIGURE 3a and 3b. Tests for chlorine source in PCDD/PCDF formation.

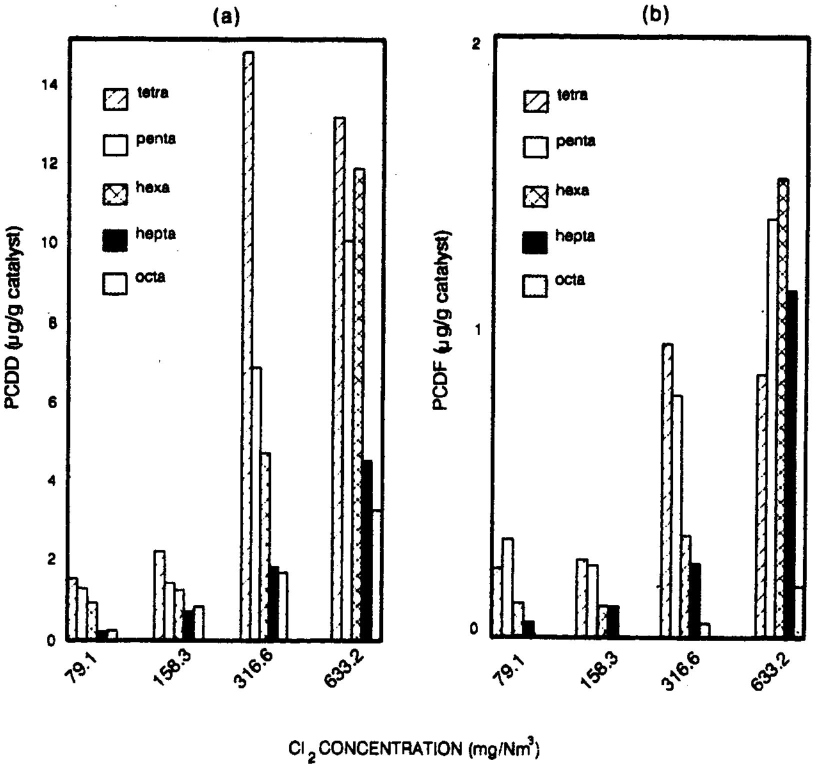

FIGURE 4a and 4b. Cl_2 concentration dependence for PCDD/PCDF formation.

DISCUSSION

The results shown in Fig. 3 (a and b) indicate that the sample run with $CuCl_2$ alone produced as much or more PCDD/PCDF as the sample with $CuCl_2$/KCl. From this it can be surmised that the KCl added to the simulated fly ash as a Cl donor in previous experiments had no enhancing effect on the reactions noted. Instead, chlorination likely occurred via Cl_2 gas formed from $CuCl_2$ decomposition. Indeed, reactions which can be expected to produce HCl from the KCl added in the Stieglitz *et al.* (3) experiments for subsequent conversion to Cl_2 require higher temperatures than those tested to occur (13). Increasing Cl_2 concentration results in greater formation of PCDD/PCDF, as shown in Fig. 4 (a and b). This accounts for the increase in PCDD/PCDF noted by Stieglitz *et al.* (3) when the amounts of $CuCl_2$ catalyst were increased in their experiments. Recalling Fig. 2, it can be seen that increasing the amount of $CuCl_2$ will result in an increased concentration of Cl_2 gas from decomposition of the catalyst.

The evidence that gas-phase Cl_2 is the source of Cl in formation of PCDD/PCDF has several implications for waste incineration. The role of the Deacon process in converting HCl to Cl_2 is essential to the formation mechanism because, although Cl_2 is thermally favored at 300 °C, it does not readily form without the presence of a catalyst, owing to kinetic limitations (8). The availability of catalytically active materials is not rare, because virtually any Cu present in fly ash can initiate the Deacon reaction. Besides CuCl and $CuCl_2$, already mentioned as Deacon catalysts, Cu, CuO, and Cu_2O all demonstrate Deacon activity (14). Research characterizing fly ash from both municipal waste (15) and hazardous waste (16) incinerators has shown that Cu is often present in the ash.

A second major implication of the role of gas-phase Cl_2 in PCDD/PCDF formation is its relationship to the concentration of HCl formed during incineration. Gullett *et al.* (14) demonstrated a first order dependency on HCl concentration for formation of Cl_2. Because PCDD/PCDF formation is linked to Cl_2 concentration, it must in turn be a function of HCl concentration. Some Cl_2 can be expected to form from decomposition of metal chlorides, such as $CuCl_2$, as in the described experiments. The potential for Cl_2 formation through the Deacon process is greater, however, owing to the continuous supply of HCl for the reaction from combustion of Cl-containing organic wastes and from high-temperature reactions with inorganic chlorides (17). This serves to continuously supply the catalyst with HCl. As mentioned above, a broader range of Cu-based metals are able to initiate catalytic conversion of HCl to Cl_2 as well.

Some researchers have indeed been able to correlate chlorinated organic formation in incinerators with measured concentrations of HCl (18); however, others have noted no connection (19). Correlation of formation with any one incinerator parameter is difficult at best, because formation can be shown to be dependent on at least four variables. First, a residence time profile in the formation temperature window (250–350 °C) sufficient to allow the reactions to take place must exist. Second, HCl must be present for conversion to Cl_2. Third, the incinerator fly ash must contain Cu-based catalysts to promote this conversion, and last, a C source must be present. Variability in incinerator operation affecting any of these parameters, such as the amount of Cu in the waste feed or the effect of combustion conditions on residual C, makes comparison between incinerators difficult.

The parameters impacting formation of PCDD/PCDF may also supply answers to control of formation in waste incinerators. In theory, eliminating one of the necessary parameters should preclude formation. Minimizing the time that fly ash spends in the formation temperature window is a simple solution. However, the kinetics of formation are not well understood at present, and it is not clear how short a time is necessary to prevent formation. Furthermore, this window coincides with heat exchangers or particle collection systems in many existing incinerators and cannot be altered inexpensively. Good combustion control will minimize C available for PCDD/PCDF formation, but does not completely eliminate formation (20), especially in times of incinerator upset. Controlling the makeup of the waste material to reduce Cu is also difficult.

Some control over the amount of HCl available for conversion to Cl_2 is possible, however. Reaction of HCl with sorbent species in the combustion zone allows its removal prior to reaching the temperatures at which the Deacon process is active, avoiding or reducing the conversion to Cl_2 necessary for formation of PCDD/PCDF. Pilot scale experiments (14) have shown that nearly all the HCl can be removed in the high-temperature zone (approximately 1,000°C) using the addition of either $CaCO_3$ or $Ca(OH)_2$. Indeed, Takeshita and Akimoto (21) have demonstrated the use of high temperature (900°C) addition of dolomite ($CaCO_3{\cdot}MgCO_3$) to reduce PCDD/PCDF formation in municipal waste combustion, and Haney (22) describes use of $CaCO_3$ to accomplish the same task in a hazardous waste incineration application.

CONCLUSIONS

The results of the experiments described in this paper give strong support to a PCDD/PCDF formation mechanism involving Cl_2 as the intermediate reactant responsible for chlorination. Results of previous formation experiments in which the Cl source was identified as an alkali salt such as KCl have been shown to have proceeded via formation of Cl_2 by decomposition of the added $CuCl_2$ catalyst. The major source of Cl participating in formation of PCDD/PCDF in waste incineration is likely therefore to be HCl (formed by combustion of Cl-containing organic wastes and high-temperature inorganic reactions) which is converted to Cl_2 by the Deacon process. Control of the HCl concentration by sorbent injection at temperatures above the Deacon process (300–550 °C) and PCDD/PCDF formation windows (250–350 °C) will reduce the formation of Cl_2 and will likely reduce the formation of PCDD/PCDF.

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