



Formation of chlorinated hydrocarbons from the reaction of chlorine atoms and activated carbon

Lavrent Khachatryan, Barry Dellinger *

Department of Chemistry, Louisiana State University, Choppin Hall 413 Baton Rouge, LA, 70803, USA

Received 5 August 2002; received in revised form 10 January 2003; accepted 19 February 2003

Abstract

The reactions of chlorine atoms and activated carbon have been studied over the temperature range of 200–400 °C using an isothermal flow reactor in conjunction with 337 nm laser photolysis of Cl₂. These studies have shown that carbon tetrachloride is the major product, with chloroform, methylene chloride, and methyl chloride being formed in progressively decreasing yields. Trace quantities of methane, ethane, and dichloroethylenes were also observed. Mechanisms of carbon fragmentation by successive addition of chlorine atoms are proposed. The formation of small chlorinated hydrocarbons by the direct reaction of chlorine with carbon may be a key link in both the de novo and precursor pathways of formation of PCDD/F.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Carbon lattice; Adsorption; Photolysis; Irradiation; Pollutants; Chlorinated hydrocarbons; VOC; PCDD/F

1. Introduction

The mechanism of formation of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F) in combustion sources has been the subject of much controversy (see, e.g., Karasek and Dickson, 1987; Stieglitz et al., 1991; Dickson et al., 1992; Addink and Olie, 1995; Sidhu et al., 1995; Milligan and Altwicker, 1996). One issue has been the mechanism of the so-called fast de novo pathway in which the presence of a flame upstream of a fly-ash bed results in more rapid formation of PCDD/F than is observed when the fly-ash bed is heated without the presence of flame (Fangmark et al., 1994). The implication of the reported studies is that reactive species generated in the flame react with the carbon in the fly-ash to form PCDD/F (Dellinger and Taylor, 1998;

Taylor et al., 1998). Because of the complexity of the effluent from a flame and the poorly characterized nature of fly-ash, identification of the responsible reactants has been difficult. Consequently, we have chosen to study the reactions of carbonaceous beds with flame-generated radicals such as ·OH, Cl·, H·, and O·.

Our results and postulated mechanism of interaction of hydroxyl radicals with carbonaceous material were reported elsewhere (Khachatryan and Dellinger, 2002). Methane, ethylene, acetylene and propylene were volatile organic compounds (VOCs) formed from the interaction of ArF laser generated hydroxyl radicals with activated carbon in the temperature range from ~200 to 450 °C. The formation of these unsaturated hydrocarbons is significant in that these species can be chlorinated by a transition metals (Taylor et al., 1998) and undergo further reaction to form chlorinated aromatic species and PCDD/F (Froese and Hutzinger, 1996).

The reactions of molecular chlorine and carbon have been previously studied. It was established that the reaction is complex and may proceed by multiple pathways (Puri et al., 1963, 1966, 1972, 1978a,b; Puri and

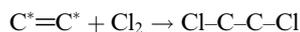
* Corresponding author. Tel.: +1-225-578-6759; fax: +1-225-578-4936.

E-mail address: barry.dellinger@chem.lsu.edu (B. Dellinger).

Bansal, 1966; Puri and Seghal, 1967; Demidovitch et al., 1968; Nikitina et al., 1969; Koltsov et al., 1973; Tobias and Soffer, 1985; Barton et al., 1987; Fedorov, 1997). A study of the reactions of molecular chlorine with various carbons indicated that, as a result of the high activity of molecular chlorine, chlorine is fixed on the surfaces of carbon over a wide range of temperatures (Puri et al., 1963, 1966, 1972, 1978a; Puri and Bansal, 1966; Puri and Seghal, 1967; Koltsov et al., 1973; Tobias and Soffer, 1985; Tobias and Soffer, 1985).

Various chlorination reactions have been proposed (exclusive of physisorption) (Puri et al., 1963, 1966, 1972, 1978a; Puri and Bansal, 1966; Puri and Seghal, 1967; Tobias and Soffer, 1985; Tobias and Soffer, 1985).

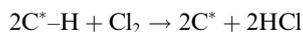
- (1) Addition, saturation of bonds of olefinic character, leading to net Cl_2 uptake,



- (2) Exchange with chemibound hydrogen



- (3) Dehydrogenation of the surface



where the symbol C^* denotes a surface carbon atom.

The reported studies focused on the formation of HCl with little emphasis on the formation of organic species or pollutants (Tobias and Soffer, 1985; Barton et al., 1987). Only carbon tetrachloride and hexachloroethane formation have been reported at 400 °C (Koltsov et al., 1973).

Experimental laboratory studies suggest that the gas–solid reaction of molecular chlorine does not appreciably impact the yields of PCDD/F via the de novo formation pathway (Stieglitz et al., 1991). However, recently reported calculational models indicate that chlorine atoms can exist in the cool-zone region of combustors (Procaccini et al., 2000).

Atomic chlorine is quite reactive and therefore may react with the surface of carbonaceous material to form species that can continue to react and form PCDD/F. However, products of direct interaction and the mechanisms of the reaction of chlorine atoms or chlorine molecules with carbonaceous material in the formation of PCDD/F is still unclear.

In this manuscript, we report and compare the results of our study of the interaction of photolytically generated chlorine atoms and molecular chlorine with activated carbon under similar conditions. This simple system is used as a model for the reaction of flame-generated chlorine atoms and carbonaceous fly-ash in combustion and thermal devices.

2. Experimental

Two grams of the purified, activated carbon pellets (o.d. ~0.8 mm) were placed in a quartz boat (20 × 50 mm) inside a cylindrical, glass tubular reactor (i.d. = 3 cm, $L = 30$ cm) (Khachatryan and Dellinger, 2002). Chlorine atoms were produced by the 337 nm photolysis of diluted (0.1%) mixture of Cl_2 in N_2 using a pulsed N_2 laser operated at 10 Hz (Lambda Physics, average power of 0.03 W at 10 Hz). For the exposures, a gas mixture of $\text{Cl}_2 + \text{N}_2 + \text{He}$ was flowed over the carbon at a velocity of 4 cm/s with the laser radiation focused just above the surface of the pellets. Cl atoms exposures were performed from 200 to 500 °C along with suitable blanks with/without laser radiation or $\text{Cl}_2 + \text{N}_2$.

Light gas and semi-volatile products were trapped cryogenically and analyzed by GC-FID and GC-MS. Chromatographic separation and analyses of light, gas-phase products (i.e., methane, olefins, acetylene) was achieved using a GC-FID (Hewlett Packard, 5890 mode, Series II) system equipped with a 30 m length, i.d. ~0.534 mm alumina column. Chlorinated hydrocarbons were analyzed using a 30-m, 0.25-mm-ID DB-5 capillary column and Ion Trap GC-MS Saturn 2000. The mass selective detector was scanned from 40 to 500 amu.

The activated carbon (Aldrich Chemical) used in this study had an elemental composition of: C—86.7 (%), H—2.98 (%), N—0.38 (%), S—0.34 (%), O and ash—9.61(%) (as difference from 100 (%)).

To remove heavy organic impurities, the activated carbon was subjected to a 17 h Soxhlet extraction with methylene chloride prior to use. Polynuclear aromatic hydrocarbons (PAH) with less than five rings are preferentially desorbed with methylene chloride (Lahaye and Prado, 1983). More strongly adsorbed PAH were extracted with toluene with an additional 17 h Soxhlet extraction. GC-MS analysis of the final extracts did not reveal appreciable quantities of heavy organic species. The pellets were then further purified and activated by exposure to flowing air at 425 °C for 5 h followed by heating at 500 °C in vacuum for 5 h.

High purity helium was used in the studies. However, it was found that that gas stream contained ppb levels of propane and propylene. This required purification of the helium by passing the gas through an activated carbon bed, followed by a liquid nitrogen trap.

At some of the experimental temperatures, carbon dioxide was formed as a result of reaction of oxygen containing surface groups with chlorine (Hall and Holmes, 1992). Formation of carbon dioxide as well as hydrogen chloride was determined by collection of a portion of the reactor effluent in an IR cell which was then subjected to FTIR analysis using a MIDAC spectrometer.

The activated carbon was subjected to treatment with the gas mixture of $\text{Cl}_2 + \text{N}_2 + \text{He}$ as long as measurable

quantities of HCl and CO₂ were released. Because HCl is adsorbed rapidly and strongly in the pores of the carbon, (Tobias and Soffer, 1985; Pasquevich, 1990), it was necessary to continue to pump the reactor for 6 h following completion of the exposure to ensure that all of the HCl was released from the carbon.

Electron spectroscopy for chemical analysis (ESCA) was used to determine the nature of possible binding of chlorine to the surface of the carbon (Papirer et al., 1978). The analyses were performed with a modified AEI ES-100 Spectrometer using Mg K α X-rays of 1253.6 eV energy at 120 W power and a pressure of $\sim 1.3 \times 10^{-5}$ Pa. The pass energy of the spectrometer was set to 65 eV for high resolution scans and 130 eV for 1000 eV wide survey scans. The instrument resolution was 1.3 eV for the full width at half maximum height of the gold ⁴F_{7/2} line. The binding energy scale was calibrated by setting the Au ⁴F_{7/2} and Cu ²P_{3/2} peaks at 84.0 and 932.6 eV, respectively. The samples were distributed on adhesive tape so as to achieve uniform and complete coverage.

3. Results

Low molecular weight chlorinated hydrocarbons were formed from exposure of the activated carbon to chlorine, both with and without laser irradiation. However, the yields were increased by greater than a factor of ~ 2.5 with exposure to laser irradiation (cf. Fig. 1). This increase is attributable to the increased ratio of chlorine atoms to molecular chlorine induced by irradiation.

Carbon tetrachloride was the dominant product with lesser quantities of C₁ chlorinated hydrocarbons and trace quantities of methane and C₂ species:

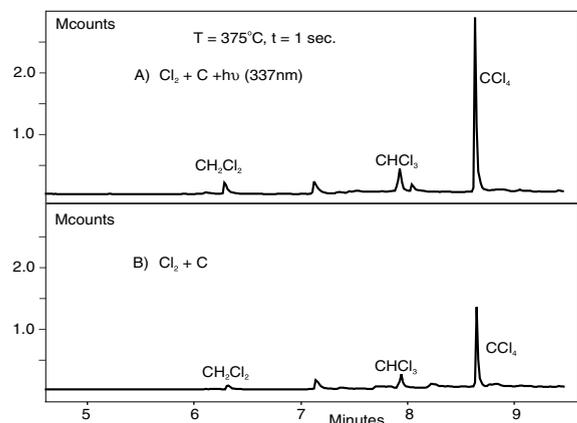
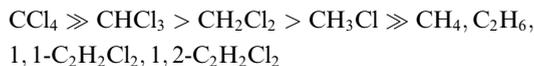


Fig. 1. Total ion current chromatogram of chlorinated hydrocarbons in the effluent resulting from the exposure of activated carbon to chlorine at 375 °C: (A) with 335 nm laser irradiation, and (B) without laser irradiation.



The net concentrations (corrected for background without laser irradiation) of all chlorinated products increased with temperature to a maximum at 340 °C and decreased until there was negligible net production at 400 °C (cf. Fig. 2). The chlorinated olefins were detected only at the maximum of the accumulation curve of chlorinated hydrocarbons.

ESCA analyses of the untreated and treated carbon were performed to determine the nature of interaction of chlorine atoms with the carbon lattice, gain insight into the pathways of carbon fragmentation, and better understand the mechanisms of formation of observed VOCs and chlorinated hydrocarbons. Evidence of the interaction of chlorine with the surface of the carbon is indicated by the results of ESCA analysis presented in Fig. 3 for the 337 nm irradiated samples. The peak at 200 eV is attributed to the presence of a chlorine atom on the surface, while the peak at 286.2 eV is attributable to carbon.

Fig. 4A and B are comparative ESCA spectra of carbon at different environments when the activated carbon was exposed to $\cdot\text{OH}$ (Fig. 4A) and Cl^\cdot (Fig. 4B), respectively. The carbon peaks (1a and 1b) are asymmetric, indicating the presence of carbon atoms in different chemical environments. Deconvoluted C1s spectra show significant concentrations of a several forms of oxygen (curves 2 and 3 in Fig. 4A and B). The higher energy shoulder can be attributed to $-\text{C}-\text{O}$ (curves 2a or 2b, at ~ 286.9 eV) and $-\text{C}=\text{O}$ (curves 3a or 3b, at ~ 288.5 eV) binding. A less intense peak appears in Fig. 4B only (curve 5, at ~ 286.2 eV, Fig. 4B) and is attributable to a $\text{C}-\text{Cl}$ moiety formed by interaction of Cl^\cdot with the activated carbon.

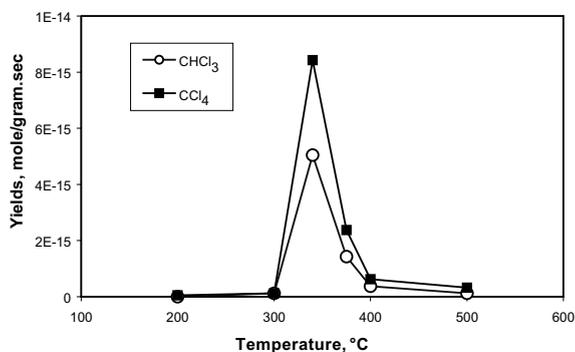


Fig. 2. Temperature dependence of the net yields of chlorinated hydrocarbons (major chlorinated hydrocarbon products) formed from the reaction of 337 nm irradiated Cl₂ with activated carbon (residence time 1 s). Yields are presented as the difference in yields of the chlorocarbon for control experiments (without laser radiation) and experiments with laser radiation.

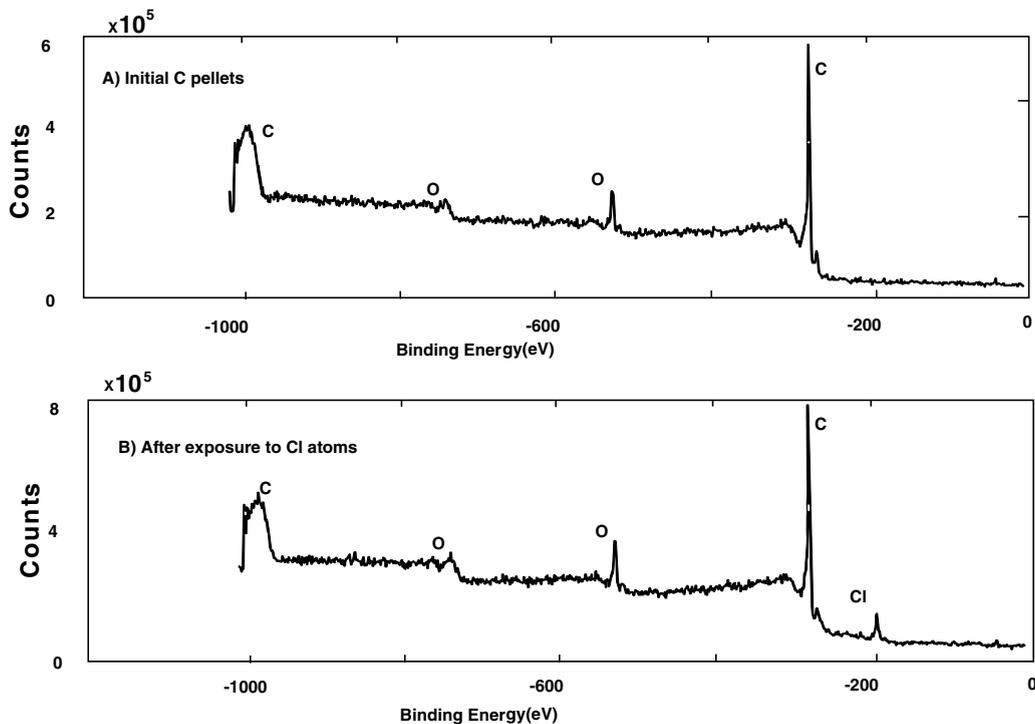


Fig. 3. Representative ESCA survey scan of C 1s (main peak at ~ 284.8 eV), O 1s (~ 532 eV) and Cl 2p (~ 200 eV) spectra. The peaks at ~ 1000 and ~ 750 eV are C KLL and O KLL Auger peaks, respectively.

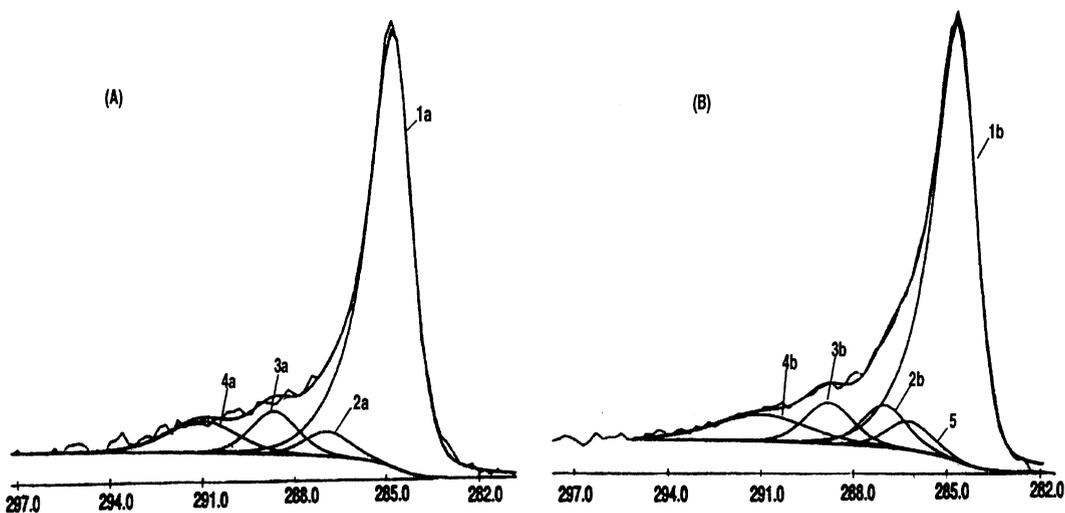


Fig. 4. Deconvoluted ESCA spectra of C 1s following exposure to hydroxyl radicals and chlorine atoms: (A) activated carbon, nitrous oxide in He, water, 193 nm laser radiation and (B) activated carbon, chlorine gas in He, 337 nm laser radiation. Curves 1–4 (a and b) and 5 are deconvolutions of the features contained in the total ESCA spectrum (see text).

Evidence of the interaction of hydroxyl radicals and chlorine atoms with the carbon lattice can be found in the data presented in Table 1 for the surface composition of activated carbon before and after laser irradiation. The ESCA results indicate that there is more C–O

and C=O carbon (and less C–C and/or C–H) carbon following exposure to either OH^\cdot or Cl^\cdot .

The shape and deconvoluted spectra of initial carbon is exactly the same for the samples after interaction with OH^\cdot or Cl^\cdot (cf. Fig. 4A and B). The only differences in

Table 1
Approximate atom % surface composition of activated carbon as determined by ESCA

	C			O			Cl
	C=O	C–O or C–Cl	C–H, C–C	–OH	O–C	O=C	Cl–C
Untreated carbon	6.3	3.6	81.1	1.6	3.5	3.9	–
Carbon + ·OH ^a	7.2	6.9	72.7	1.7	5.3	5.7	–
Carbon + Cl ^b	5.4	8.6	69.2	1.5	4.5	6.0	5.0

^a He/H₂O/N₂O mixture was photolysed by ArF excimer laser at 193 nm ([N₂O]:H₂O = 20:1). Photolysis of N₂O produced O (¹D) atoms that quantitatively reacted with water to produce hydroxyl radicals (Khachatryan and Dellinger, 2002).

^b Cl₂ was photolysed with an N₂ laser at 337 nm to produce chlorine atoms.

the oxygen content between the OH[–]-exposed and Cl[–]-exposed samples are that peaks 2 and 3 are more intense for the samples that reacted with OH[–]. This suggests that exposure of the carbon lattice to Cl[–] activates the lattice to reaction with residual adsorbed oxygen species.

Additional evidence of destruction of the carbon lattice is obtained by comparison of the characteristics of the graphitic carbon π – π^* shake-up satellite peak (cf. curves 4a and 4b in Fig. 4) before and after exposure to the reactive radicals. The relative intensity of the π – π^* shake-up satellite peak at \sim 291 eV is greater on the “initial carbon” sample than on the exposed samples. Since this shake-up satellite is characteristic of graphitic carbon, this result indicates that there is less exposed graphite following irradiation.

4. Discussion

4.1. Mechanism of formation of volatile chlorinated hydrocarbons

It has been reported that carbon has a catalytic effect on the dissociation of Cl₂ into chlorine atoms that can

be detected in the gas phase (Amorebieta and Colussi, 1985). Interaction of chlorine with activated carbon is characterized by the localized adsorption and formation of strongly paramagnetic, carbon–chlorine charge-transfer complexes, i.e. C⁺ ··· Cl₂[–] (20–300 °C) and C⁺ Cl[–] (300–400 °C) which can apparently result in the liberation of gas-phase chlorine atoms (Koltsov et al., 1973; Fedorov, 1997).

Laser irradiation increases the concentration of chlorine atoms through photodissociation of molecular chlorine. In our experiments, this increase in chlorine atom concentration intensifies the process of chlorination of carbon without changing the product distribution. CCl₄, CHCl₃, and the other observed chlorinated hydrocarbons are themselves important environmental pollutants.

Simple pathways to formation of CCl₄ are depicted in Schemes A and B in Fig. 5. The most probable carbon sites for initial attack by Cl (or Cl₂) are distorted graphitic π bonds and acetylenic units (Demidovitch et al., 1968; Tobias and Soffer, 1985). The existence of the super-active sites have been suggested at low temperatures (up to 220 °C) that may be rapidly annealed out at higher temperatures, 450–550 °C (Ismail and Walker, 1989).

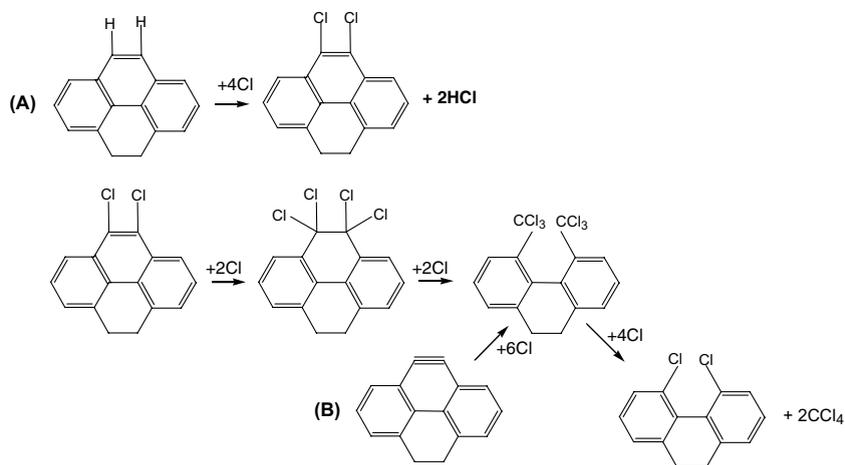


Fig. 5. Proposed pathways to formation of carbon tetrachloride.

Acetylenic active sites, such as overstressed quasi-acetylene bonds have concentrations as high as 10^{15} cm^{-2} (Demidovitch et al., 1968; Nikitina et al., 1969). In both cases the sequential attack of the Cl (or Cl_2) occurs at these overstressed bonds eventually resulting in bond rupture and elimination of CCl_4 into the gas phase.

Formation of CHCl_3 can be explained by Scheme A when the full exchange of chemibound hydrogen on the olefinic π bonds (carbon basal plane) does not take place. Similar arguments may be applied to the formation of CH_2Cl_2 and CH_3Cl . However, traces of CH_2Cl_2 and CH_3Cl may also be accounted for by the chlorination of surface-bound methyl groups or methane which is released from the carbon surface. The source of methane can be small amounts of methyl groups attached to the carbon lattice which are detached by the attack of chlorine atoms. The mechanism of formation from methyl groups or methane in the early stages of treatment is supported by the observation that the concentrations of methane, ethane, CH_2Cl_2 and CH_3Cl decrease gradually with sequential exposure of the activated carbon to chlorine.

4.2. Implications for formation of PCDD/F and other pollutants

The formation of the observed C_1 chlorinated hydrocarbons may be highly significant in the formation of other pollutants, including PCDD/F. We have previously demonstrated that these same species undergo homogeneous, gas-phase molecular growth reactions at reaction times of 2.0 s and temperatures in the range of 600 °C to form higher molecular weight species such as trichloroethylene, tetrachloroethylene, and hexachlorobenzene (Taylor et al., 1991). We have also shown that trichloroethylene and tetrachloroethylene undergo copper catalyzed molecular growth and condensation reactions to form hexachlorobenzene and PCDD/F at in the temperature range of 200–600 °C (Taylor et al., 1998). Related research in our laboratory has also shown that the presence of catalytic surfaces, such as alumina and iron oxide, decreases the reaction temperature for CCl_4 by as much as 350–400 °C (Abbas and Dellinger, 2002).

We have hypothesized that a more transient species, such as radicals and atoms produced in the high-temperature region of the flame, attacked the carbonaceous components of the fly-ash to produce PCDD/F or precursors (Dellinger and Taylor, 1998; Taylor et al., 1998). This led to our previously reported study of the formation of olefins and acetylenes from the reaction of hydroxyl radical with carbon pellets (Khachatryan and Dellinger, 2002). The results reported in this manuscript demonstrate that chlorine atoms can also react with carbon to form chlorinated hydrocarbons directly without the intermediate, metal catalyzed chlorination reaction. These chlorinated hydrocarbons can undergo

further molecular growth reactions leading to formation PCDD/F as suggested earlier (Dellinger and Taylor, 1998).

Reaction kinetic models support the somewhat surprising contention that chlorine atoms formed in the flame by decomposition of chlorinated hydrocarbons, hydrogen chloride, or molecular chlorine can survive in the post-flame region of a combustion system sufficiently long to attack carbonaceous material (Procaccini et al., 2000). These modeling calculations indicate that chlorine atoms can be 1–5% of the total chlorine at temperatures as low as 500 K. The high molar ratios of $[\text{Cl}]/[\text{C}] \sim 0.0052$ and $[\text{Cl}]/[\text{H}] \sim 0.0032$ in flue gases of a municipal solid waste incinerator (Babushok et al., 2000) suggests that chlorine atoms, versus the more reactive hydroxyl radicals, can play a major role in the post-combustion formation of PCDD/F.

The ability to form carbon tetrachloride and other C_1 chlorinated hydrocarbons in the post-flame region is important to the pathway because these species are thermally fragile and unlikely to survive if they are formed as products in the flame (Dellinger and Taylor, 1998; Taylor et al., 1998; Taylor and Dellinger, 1999). Post-flame formation ensures that their concentration remains high and they have the opportunity to undergo further surface catalyzed reactions to form PCDD/F. The observed temperature range of formation and the optimum temperature of formation, i.e. $\sim 330\text{--}340$ °C, agrees favorably with the temperature range reported for PCDD/F formation reported in full-scale combustors (Fiedler, 1998; Xhrouet et al., 2001), suggesting that the chlorine-carbon reaction might be rate controlling.

5. Summary

The formation of chlorinated hydrocarbons, predominantly carbon tetrachloride was established by the study of the reaction of laser-generated chlorine atoms with activated carbon at temperatures as low as 200 °C. The results reported in this manuscript demonstrate that chlorine atoms can react with carbon to form chlorinated hydrocarbons directly without an intermediate, metal catalyzed chlorination reaction. Additionally, chlorine is fixed on the surfaces of carbon over a wide temperature range. This simple system is used as a model for the reaction of flame-generated chlorine atoms and carbonaceous fly-ash in combustion and thermal devices. The formation of small chlorinated hydrocarbons by the direct reaction of chlorine with carbon may be a key link in the formation of pollutants, including PCDD/F.

These findings also raise the rather disturbing specter that many pollutants other than PCDD/F and their precursors may be forming in the post-combustion,

cool-zone regions of combustors where they can be emitted without being exposed to destructive conditions.

Acknowledgements

This research is partially supported by the US-EPA under STAR grant R-826166 and the Patrick F. Taylor Chair.

References

- Abbas, K., Dellinger, B., 2002. FTIR investigation of adsorption and chemical decomposition of CCl_4 by high surface-area aluminum oxide. *Environ. Sci. Technol.* 36 (7), 1620–1624.
- Addink, R., Olie, K., 1995. Mechanisms of formation and destruction of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in heterogeneous systems. *Environ. Sci. Technol.* 29, 1425–1435.
- Amorebieta, V.T., Colussi, A.J., 1985. Direct study of the catalytic decomposition of chlorine and chloromethanes over carbon films. *Int. J. Chem. Kin.* 17, 849–858.
- Babushok, V., Tsang, W., Noto, T., 2000. Propargyl-type radicals as precursors for polychlorinated aromatic hydrocarbons during incineration. Presented at Proceedings of 28th Symp.(Int) on Combustion, Combustion Institute, Pittsburgh, 28(Pt. 2), pp. 2691–2699.
- Barton, S.S., Evans, M.J.B., Koresh, J.E., Tobias, H., 1987. The effect of chlorination on the adsorptive properties of water on carbon cloth. *Carbon* 25, 663–667.
- Dellinger, B., Taylor, P.H., 1998. Chemical aspects of combustion of hazardous wastes. *Cent. Eur. J. Public Health* 6, 79–87.
- Demidovitch, G.B., Kiselev, V.F., Lejnev, N.N., Nikitina, O.V., 1968. Nature of la surface du graphite fraichement brove et mecanisme de l'interaction de cette surface avec l'oxidation et l'hydrogene. *J. Chim. Phys.* 65, 1072–1078.
- Dickson, L.C., Lenoir, D., Hutzinger, O., 1992. Quantitative comparison of de novo and precursor formation of polychlorinated dibenzo-*p*-dioxins under simulated municipal solid waste incinerator post-combustion conditions. *Environ. Sci. Technol.* 26, 1822–1828.
- Lahaye, Ed.J., Prado, G., 1983. *Soot in Combustion Systems*. Plenum Press, New York.
- Fangmark, I., Stomberg, B., Berge, N., Rappe, C., 1994. Influence of small fly ash particles on the post-combustion formation of PCDDs, PCDFs, PCBzs, and CPs in pilot incinerator. *Chemosphere* 29 (9–11), 1903–1909.
- Fedorov, A.A., 1997. Interaction of chlorine with AGM activated carbon. *Russ. J. Appl. Chem.* (translation) 70, 44–46.
- Fiedler, H., 1998. Thermal formation of PCDD/PCDF: a survey. *Environ. Eng. Sci.* 15, 49–58.
- Froese, K.O., Hutzinger, O., 1996. Polychlorinated benzene, phenol, dibenzo-*p*-dioxin, and dibenzofuran in heterogeneous combustion reactions of acetylene. *Environ. Sci. Technol.* 30, 998–1009.
- Hall, C.R., Holmes, R.J., 1992. The preparation and properties of some activated carbons modified by treatment with phosgene of chlorine. *Carbon* 30, 173–176.
- Ismail, J.M.K., Walker Jr., P.L., 1989. Detection of low temperature carbon gasification using DSC and TDA. *Carbon* 27, 549–559.
- Karasek, F.W., Dickson, L.C., 1987. Model studies of polychlorinated dibenzo-*p*-dioxin formation during municipal refuse incineration. *Science* 237, 754–756.
- Khachatryan, L., Dellinger, B., 2002. The formation of olefins and alkynes from the reaction of hydroxyl radical and carbonaceous material. *J. Chem. Soc., Perkin Trans. 2*, 779–783.
- Koltsov, S.I., Smirnov, E.P., Aleskovskii, V.B., 1973. Interaction of chlorine with microcrystalline carbon. *Zhurnal Obshchei Khimii* (translation) 8, 1643–1647.
- Milligan, M.S., Altwicker, E., 1996. Chlorophenol reactions on fly ash. I. Adsorption/desorption equilibria and conversion to polychlorinated dibenzo-*p*-dioxins. *Environ. Sci. Technol.* 30, 225–229.
- Nikitina, O.V., Kiselev, V.F., Lezhnev, N.N., Prudnikov, R.V., 1969. Inhibiting action of the products of the surface reaction on the chemisorption of oxygen, hydrogen, and chlorine on an atomically pure graphite surface. *Kinetika i Kataliz* (translation) 10, 1148–1150.
- Papire, E., Guyon, E., Perol, N., 1978. Contribution to the study of the surface groups on carbons—II. *Carbon* 16, 133–140.
- Pasquevich, D.M., 1990. Mass effects on the surface reaction of chlorine with carbon. *Thermochim. Acta* 167, 91–98.
- Procaccini, C., Bozzelli, J.W., Longwell, J.P., Smith, K.A., Sarofim, A.F., 2000. *Environ. Sci. Technol.* 34, 4565–4570.
- Puri, B.R., Malhotra, S.L., Bansal, R.C., 1963. The formation and properties of carbon-halogen surface complexes. I. Interaction of charcoal and chlorine gas. *J. Indian Chem. Soc.* 40, 179–187.
- Puri, B.R., Tuli, S.S., Bansal, R.C., 1966. Studies in formation and properties of carbon-halogen surface complexes. II. Treatment of charcoal with chlorine gas at different pressures and stability of the carbon-chlorine complex. *J. Indian Chem.* 4 (1), 7–11.
- Puri, B.R., Bansal, R.C., 1966. Studies in surface chemistry of carbon blacks. III. Interaction of carbon blacks and aqueous bromine. *Carbon* 3 (4), 523–539.
- Puri, B.R., Seghal, K.C., 1967. Formation and properties of carbon-halogen surface complexes. IV. Stability of carbon bromine surface complex. *Indian J. Chem.* 5 (8), 379–380.
- Puri, B.R., Mahajan, O.P., Gandhi, D.L., 1972. Surface unsaturation in microcrystalline carbons. *Indian J. Chem.* 10, 848–849.
- Puri, B.R., Singh, D.D., Arora, V.M., 1978a. Adsorption of chlorine by carbons from solutions in carbon tetrachloride. *J. Indian Chem. Soc.* 55 (5), 488–491.
- Puri, B.R., Singh, D.D., Verma, S.K., 1978b. Studies in catalytic reactions of carbon: Part VII—Catalytic chlorination of toluene in presence of active carbon. *Indian J. Chem.* A 16, 1026–1029.
- Sidhu, S.S., Maqsd, L., Dellinger, B., Mascolo, G., 1995. The homogeneous, gas-phase formation of chlorinated and brominated dibenzo-*p*-dioxin from 2,4,6-trichloro- and 2,4,6-tribromophenols. *Combust. Flame* 100, 11–20.

- Stieglitz, L., Vogg, H., Zwick, G., Beck, J., Bautz, H., 1991. On formation conditions of organohalogen compounds from particulate carbon of fly ash. *Chemosphere* 23, 64–1225.
- Taylor, P.H., Dellinger, D., Tirey, A., 1991. Oxidative pyrolysis of methylene chloride, chloroform, and carbon tetrachloride. I. Incineration implications. *Int. J. Chem. Kin.* 23, 1051–1074.
- Taylor, P.H., Sidhu, S.S., Rubey, W.A., Dellinger, B., Wehrmeier, A., Lenoir, D., Schramm, K.W., 1998. Evidence for a unified pathway of dioxin formation from aliphatic hydrocarbons. Presented at 27th Symposium (International)/The Combustion Institute, Pittsburgh, PA, p. 1769.
- Taylor, P.H., Dellinger, B., 1999. Pyrolysis and molecular growth of chlorinated hydrocarbons. *J. Anal. Appl. Pyrolysis* 49, 9–29.
- Tobias, H., Soffer, A., 1985. Chemisorption of halogen on carbons—I. Stepwise chlorination and exchange of C–Cl with C–H bonds. *Carbon* 23, 281–289.
- Tobias, H., Soffer, A., 1985. Chemisorption of halogen on carbons—II. Thermal reversibility of Cl₂, HCl and H₂ chemisorption. *Carbon* 23, 291–299.
- Xhrouet, C., Pirard, C., Pauw, E., 2001. De Novo synthesis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans on fly ash from a sintering process. *Environ. Sci. Technol.* 35, 1616–1623.