PERKIN 2

The formation of olefins and alkynes from the reaction of hydroxyl radical and carbonaceous material

Lavrent Khachatryan and Barry Dellinger *

Department of Chemistry, Louisiana State University, Baton Rouge, LA, 70803, USA.
E-mail: barry.dellinger@chem.lsu.edu; Fax: 225 578-3458; Tel: 225 578-6759

Received (in Cambridge, UK) 14th November 2001, Accepted 12th February 2002
First published as an Advance Article on the web 1st March 2002

Using model systems and laser photolysis techniques, we have examined the mechanism of interaction of hydroxyl radicals with carbonaceous materials. The formation of ppb-level concentrations of methane, ethylene, acetylene, and propylene (prop-1-ene) was observed from interaction of ArF laser-generated hydroxyl radicals with activated carbon pellets in the temperature range of 200–500 °C. A maximum in the formation of olefins and acetylene is observed at 430–450 °C. A mechanism involving surface epoxide formation is postulated. These results support earlier hypotheses regarding the role of combustion generated hydroxyl radicals and light hydrocarbons in the catalytic formation of polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/F) by the so-called "fast"*de novo* and extended precursor mechanisms.

Introduction

The discovery that polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) are largely formed by surface mediated or catalyzed reactions in the post-combustion, cool-zone of combustion systems suggests that other observed pollutants may be formed in the cool-zone as well. [1–8] Reactive species that are formed in the flame and survive the combustion-zone can react with fly-ash and soot at the gas–solid interface to produce various gaseous and surface-bound species.[3,9–13] In the case of chlorine-containing systems, carbon contained in soot and fly-ash can serve as a reagent for formation of chlorinated benzenes, chlorinated phenols, PCDD/F and many other related chemicals. In studies of the so-called "fast *de-novo*" mechanism of PCDD/F formation, it has been shown that a flame placed upstream of a carbon-containing bed produces species that accelerate the rate of pollutant formation.[8] While molecular species, such as nitrogen oxides and water, may react with carbonaceous materials to produce gasified products, combustion-generated radicals are expected to be more reactive and are implicated in the mechanism of pollutant formation.[12] However, studies to date have largely used molecular reactants to study specific reactions and infer the role of radical intermediates or used flames to generate copious and poorly defined quantities of radicals and molecular reactants.

Consequently, we have chosen to study the reactions of well-characterized carbonaceous beds with flame-generated radicals, such as hydroxyl and peroxyl, as well as atoms such as chlorine, hydrogen, and oxygen. In our studies, these radicals are generated photolytically from suitable precursors to avoid complications of the possible reactions of multiple, flame-generated species. Because of its ubiquitous nature, relatively high concentration under oxidative and stoichiometric conditions, and high reactivity, our initial focus has been the reaction of hydroxyl radical ($^{\bullet}$OH). Specifically, hydroxyl radicals can react with carbonaceous solids, such as soot and fly-ash, to form simple olefinic and acetylenic hydrocarbons. These species are environmentally significant in that they can undergo molecular growth reactions to form toxic butadiene and polycyclic aromatic hydrocarbons (PAH), or in the presence of chlorine, form chlorinated benzenes, chlorinated phenols, and PCDD/F.[12,14,15]

Experimental

Activated carbon pellets were exposed to hydroxyl radicals generated by ArF excimer laser photolysis of a suitable precursor. Light gas and semivolatile products were trapped cryogenically and analyzed by GC-FID and GC-MS (*cf.* Fig. 1). The activated carbon pellets were used as a surrogate for combustion generated soot, and the photogenerated hydroxyl radical was used as a controlled replica of the combustion-generated hydroxyl radical.

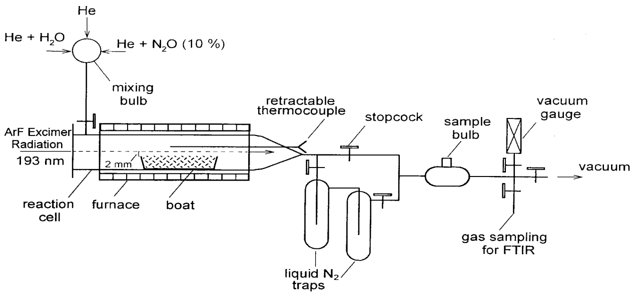


Fig. 1 Diagram of experimental apparatus.

Carbon pellets were used as a surrogate for the carbonaceous material in fly-ash because of their well defined elemental composition. The activated carbon pellets (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%).

Prior to use, the pellets were subjected to extensive purification to remove molecular species. To remove heavy organic impurities, the carbon pellets were subjected to 17 hours' soxhlet extraction with methylene chloride. PAH with less than five rings are preferentially extracted with methylene chloride.[16] To remove more strongly adsorbed PAH, the pellets were also subjected to soxhlet extraction with toluene for 17 h. GC-MS analysis of the final extracts revealed no detectable quantities of any PAH. The pellets were further purified by heating in flowing air at 425 °C for 5 h, followed by thermal treatment at 500 °C *in vacuum* for 5 h.

2.0 g of the purified carbon pellets (od ~0.8 mm) were placed in a quartz boat (20 × 50 mm) inside a cylindrical, glass tubular

DOI: 10.1039/b110371g

reactor (id = 0.3 cm, L = 30 cm). The reactor was fitted with a Suprasil 1 window suitable for ArF excimer laser irradiation at 193 nm (Lambda Physik, average power at 4 Hz ~ 0.25 W). The collimated, rectangular laser beam was aligned 2 mm above the carbon pellets.

A gas-delivery vacuum system using a standard gas manifold with controlled gas inlets was used to introduce nitrous oxide, water vapor, and helium carrier gas to the cell. The entire system was heated and insulated for operation up to 500 °C. For the exposures, a He–H_2O–N_2O mixture was flowed over the pellets with a velocity of 4 cm s^{-1} at a $[H_2O] : [N_2O] = 20 : 1$. Photolysis of N_2O produced O (^1D) atoms that quantitatively reacted with water to produce hydroxyl radicals.[17] The entire reactor system was evacuated for thirty minutes prior to introducing the reactant gas mixture. This gas mixture was passed over the carbon pellets with and without (blank experiments) laser irradiation from room temperature up to 500 °C.

Volatile products were cryogenically collected in a cryotrap at 77 K for 30 minutes. Separation of light products ($< C_5$) was achieved using a GC-FID (Hewlett Packard, 5890 mode, Series II) system equipped with a 30 m × 0.544 mm alumina column. Release of CO_2 was monitored by collection in an FTIR cell whose contents were analyzed on a MIDAC FTIR spectrometer.

Initial experiments revealed that UHP helium contained impurities at ppb levels of propylene. In the presence of the 193 nm laser radiation, propylene was 30–40% decomposed to form both ethylene and acetylene. The yields of ethylene and acetylene were independent of temperature and were not affected by the presence or absence of the carbon pellets. Consequently, it was necessary to remove the propylene from the helium by passing the gas flow through the traps filled with activated carbon immersed in the liquid nitrogen. With this modification, no propylene, ethylene, or acetylene could be detected in the helium carrier or the reactor effluent in experiments with or without laser irradiation or the carbon pellets.

We also studied the modification of the surface of the activated carbon pellets following exposure to hydroxyl radical using Electron Spectroscopy for Chemical Analysis (ESCA) techniques.[18] The analyses were performed with a modified AEI ES-100 Spectrometer using Mg Kα X-rays of 1253.6 eV energy at 120 W power and a pressure of ~1.3×10^{-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.

The EPR spectra of individual samples of carbonaceous particulate were measured using a Varian E-109 spectrometer. The EPR parameters were set at 100-kHz, X-band; microwave frequency, 9.395 GHz; attenuation, 12 dB; modulation amplitude, 2 G; time constant, 2 s; receiver gain 5000, and scan time, 4 min.

Results and discussion

The volatile products formed from the reaction of hydroxyl radical and carbon pellets were, in order of decreasing concentration, methane > ethylene > acetylene > propylene > traces of C_3 hydrocarbons (*cf.* Fig. 2). As can be seen from examination of Fig. 2, the yields of all volatile products monotonically increase from ~200 to 430–450 °C and decrease at 475 °C. Detectable quantities of carbon dioxide were observable only above 300 °C.

It should be noted that both nitrous oxide and water, like nitric oxide and carbon dioxide, are carbon gasification agents.[19–26] Although their reactivity is thought to vary as $N_2O > NO > H_2O > CO_2$, their redox reaction mechanism is thought to be similar and involve the production of hydroxyl radicals and oxygen atoms.[24–26]

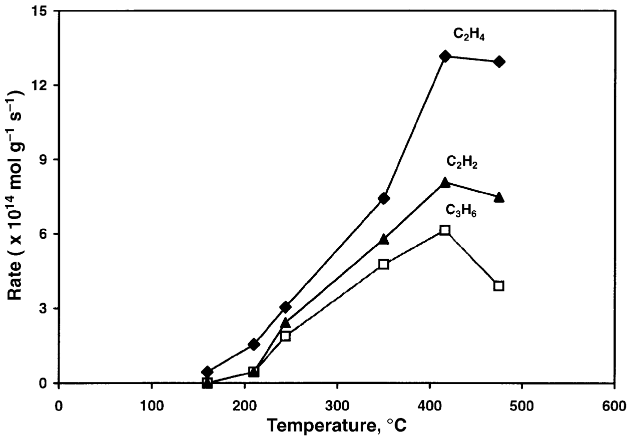


Fig. 2 Temperature dependent yields of volatile products from the reaction of excimer laser-generated $^{\bullet}OH$ and carbon.

We addressed these issues with a series of background experiments. In the absence of the 193 nm laser radiation, the yields of products with all other reactants in place were only ~10% of the yield with laser irradiation. This is evidence of the increased concentration of reactive hydroxyl radicals induced by the laser-photolysis of nitrous oxide and subsequent reaction with water (*cf.* Fig. 3).

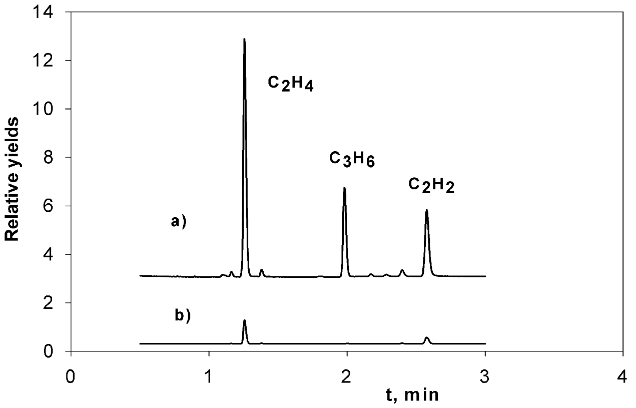


Fig. 3 Chromatograms of the reactor effluent at 330 °C showing the dependence of the yields of volatile products on reagent composition. (a) Carbon pellets, nitrous oxide, water, 193 nm laser radiation. (b) Carbon pellets, nitrous oxide, water.

It was noted that when the experiments were conducted for periods of greater than one hour, an inhibition effect appeared as the rate of formation of olefins and carbon dioxide decreased by a factor of 1.5–2. The inhibition may be associated with changes in the physical, surface characteristics of the carbon pellets and a reduction in the number of reactive sites. Consequently, quantitative experiments were conducted for a duration of 0.5 hour. The observation of this inhibition effect may have consequences for the yields of PCDD/F from fresh *versus* aged fly-ash.

The carbon pellets were also subjected to EPR analysis before and after exposure to hydroxyl radical. Prior to exposure to hydroxyl radical, the carbon pellets at the upper surface layer of the sample exhibited an EPR signal consistent with the presence of a paramagnetic center. The EPR signal was symmetrical and very weak with $g = 2.0011$. Impurity centers can give rise to characteristic EPR spectra which are, however, extremely difficult to characterize and interpret.[27]

The small g-factors are consistent with signals due to traces of metals (ppm level) in the carbon with F centers (trapped electron centers at vacancies).[28,29] This signal disappeared upon

Table 1 Elemental composition of some carbon-containing particulate matter (weight %)

	Fixed carbon	H	N	S	O	Ash	Ref.
Graphite	99.06	0.05	0.01	0.62	0.1	0.16	21
North Dakota char (lignite)	64	4.6	1,5	0.5	18.0	11.4	30
Rosebud char (subbituminous)	62.8	4.4	1.0	1.3	15.9	14.7	30
KY 13 char (bituminous)	73.7	4.8	1.9	1.4	10.1	8.1	30
Activated carbon Norit RB1 pellets	86.67	2.98	0.38	0.34	9.61[a]		This work
Fly-ash	~4	Si (16.6) Na (2.0)	Ca (8.9) Zn (1.16)	Al (8.2) Mg (1.3)	K (3.3) Cu (0.11)	Fe (3.0)	31

[a] % [O + ash] obtained as difference from 100%. Elemental analysis was performed on the purified carbon pellets.

exposure to hydroxyl radical, indicating the direct interaction of the hydroxyl radical with active sites on the carbon.

It is pertinent to note that the EPR spectra of the carbon pellets from bottom layers did not change during exposure, indicating that interactions of $^{\bullet}OH$ occur primarily with the pellets on the upper surface of the sample.

In Table 1 the elemental compositions of municipal waste incinerator fly-ash, graphite, and chars from coal are compared with the composition of the carbon pellets used in this study. As can be seen from the table, the fixed carbon, H, and O/ash concentrations for the activated carbon pellets are in the middle of the range for various coals.[21,30,31] Municipal incinerator fly-ash has a 15 to 20 fold lower carbon concentration and relatively high concentrations of silicon, metals, and transition metals.[31] Although the carbon component of fly-ash is not nearly as well characterized as in coals, the carbon pellets used in this study appear to be an appropriate surrogate for gasification in the absence of metals. The role of metals will be the subject of future investigations.

Most of the work reported in the literature concerning the gasification of carbon involves reactions with molecular species, *i.e.* hydrogen, carbon dioxide, water, nitrous oxide, nitric oxide, oxygen *etc.*[19–22,32] More limited work has been reported on gasification by radical species, *viz.* oxygen atoms and hydrogen atoms.[33–35]

Several mechanistic interpretations have been suggested.[19,20,22,33,34] Because of the higher energy of vacancies and defects relative to the bulk surface, when the surface of graphite is exposed to reacting gases at high temperature, gasification reactions are initiated at vacancies or reactive defects by removing the atoms surrounding these sites.[23] Various experiments have shown that atoms and radicals probably have a degree of mobility on the surface[22] and can recombine to give observed products. In one view, the distribution of all the primary products (saturated and unsaturated) depends on the competition between the rates of abstraction of hydrogen (from hydrogen-containing gas-phase products), dimerization of the intermediate radicals (adsorbed on the surface), and desorption of the product molecule.[19,20]

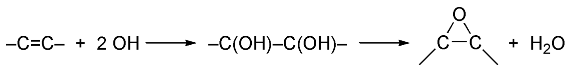
Recently, a unified mechanism (based on molecular orbital calculations) has been proposed for the gasification reactions of graphite by oxygen containing gases such as CO_2, H_2O, NO, and N_2O in both catalyzed and uncatalyzed systems.[24–26] In this mechanism, there are two types of oxygen intermediates that are bonded to the active edge carbon atoms: an in-plane semiquinone-type species and an out-of-plane epoxy group. (Carbonyl intermediates may also be involved). Calculations indicate that the edge C–C bonds are substantially weakened by ~33% when one of the edge carbons is bonded to an oxygen atom. The rate-limiting step in gasification is the rupture of C–C bonds adjacent to the semiquinone (followed by liberation of CO from the semiquinone intermediate).

It might be expected that the gasification of carbon with atoms and radicals (O, H, Cl, N, $^{\bullet}OH$, $^{\bullet}CH_3$, *etc.*) may proceed more rapidly than with the molecular species discussed above. Kinetic studies of the oxidation of three amorphous carbons and graphites by atomic oxygen clearly established that the gasification rate by oxygen atoms is much higher than by oxygen molecules.[33] If the rate controlling step in the gasification of carbon by molecular oxygen is dissociative chemisorption, then the rate controlling step in the gasification by atomic oxygen is the formation of the carbon–oxygen activated-complex.

In studies on the relative importance of H_2O, CO_2, O_2, O and $^{\bullet}OH$ in soot oxidation and gasification, it was concluded that the hydroxyl radical is the principal oxidant of soot.[35–38] However, atomic oxygen is considered as the species responsible for creating vacancies on the carbon surface, regardless of the initial oxidant.[24–26]

On the basis of the available literature and our experimental data, we postulate two pathways of hydroxyl radical interaction with carbon that can ultimately lead to the observed products:

1. Direct attack on the unsaturated C=C bonds and the resultant formation of surface epoxy groups *via* elimination of water.



2. Dissociative chemisorption at the active carbon sites, which are the edge carbon atoms on the armchair and zigzag faces. Oxygen atoms released in this reaction can also form the epoxy oxygen intermediate.

$$^{\bullet}OH \Leftrightarrow O_{ads} + H_{ads}$$

Evidence of the interaction of hydroxyl radicals with the carbon lattice can be found in the data presented in Table 2 for the surface composition of carbon pellets before and after laser irradiation. The ESCA results show that there is more oxygen and less C–C (and/or C–H) carbon on the exposed sample than on the unexposed sample. It is interesting to note the formation of "new" C–O or C=O bonds on the surfaces after exposure to hydroxyl radicals.

Fig. 4 presents possible mechanisms for the formation of methane, ethylene, and propylene in our system. In these schemes, methane, ethylene, and propylene are formed from the graphite, zigzag form of carbon. Our system exclusively contains $^{\bullet}OH$, and therefore we cannot invoke the common mechanism of methane formation involving sequential additions of H_{ads} to $(CH_n)_{ads}$ groups.

Since most forms of carbon contain hydrocarbon chains attached to the graphite structure[36,39] *ipso* addition of OH at the site of methyl substitution (II in Fig. 4), followed by migration of the hydrogen to the methyl group, forms methane and a surface bound semiquinone (*cf.* left-hand path of Fig. 4). Invoking the role of a methyl group also facilitates development of a mechanism for the formation of propylene.

A mechanism for the formation of ethylene and propylene is depicted on the right side of Fig. 4. The initial step in their formation is dissociative chemisorption of $^{\bullet}OH$ at an edge carbon to form epoxides (III in Fig. 4). Based on discussions in the literature, the rate determining step is the breaking of two

Table 2 Approximate atom (%) surface composition of carbon pellets, as determined by ESCA

Sample	C			O		
	C=O	C–O	C–H, C–C	–OH	O–C	O=C
Initial carbon	6.3	3.6	81.1	1.6	3.5	3.9
Carbon exposed to OH	7.2	6.9	72.7	1.7	5.3	5.7

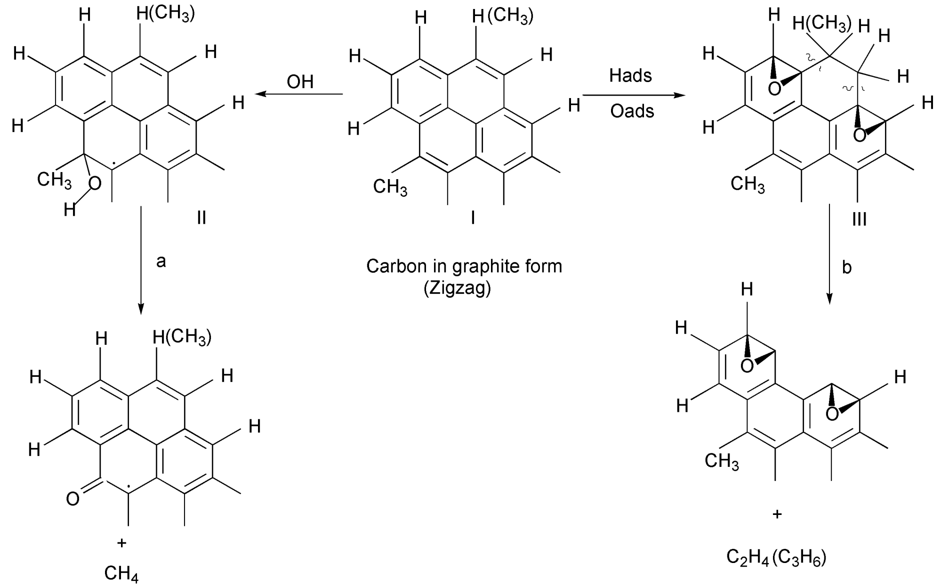


Fig. 4 A possible mechanism for formation of methane, ethylene, and propylene from the reaction of hydroxyl radical and the zigzag form of carbon. The left hand side depicts methane formation *via* hydroxyl radical addition. The right hand side depicts ethylene or propylene formation by dissociative chemisorption of hydroxyl radical.

weakened C–C bonds (signified by C ~ C), with liberation of ethylene or propylene. If one of the sites is methyl substituted, then propylene is formed; if not, then ethylene is formed. The product distribution ($[CH_4]/[C_2H_4 + C_3H_6] \sim 15$) indicates that carbon lattice destruction (formation of olefins) by dissociative chemisorption of $^{\bullet}$OH is less facile than detachment of a methyl substituent by addition of $^{\bullet}$OH.

The conventional mechanism of C_2H_2 formation through the reaction of two $(CH)_{ads}$ radicals does not appear to be important in our system, as the reaction is reported to occur at temperatures greater than ~700 °C.[33] However, two alternative mechanisms for formation of acetylene can be readily envisioned from the chair form of carbon (*cf.* Fig. 5) while formation from the zigzag form is less evident.

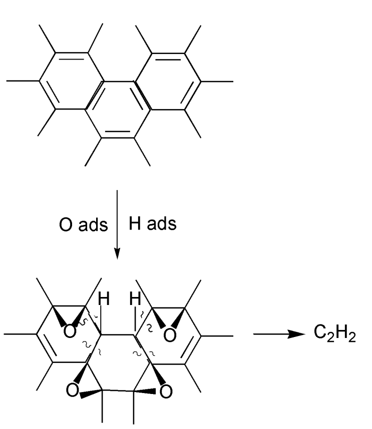


Fig. 5 A proposed mechanism for formation of acetylene from the dissociative chemisorption of hydroxyl radical with the armchair form of carbon.

In one postulated mechanism, four $^{\bullet}$OH are dissociatively chemisorbed to form epoxides and weakened C–C bonds. These bonds rupture to liberate an acetylene molecule. (A five bond cleavage sequence has been previously proposed to account for butane formation in the hydrogen–graphite reaction[40]). It is important to note that there is a reactivity difference between two surface orientations: the zigzag and armchair (basal) forms of carbon. For instance, the hydrogen atom sticking probability (physical or chemical adsorption) is about three times larger on the prism plane (zigzag) than on the basal plane.[35]

Reaction of $(CH)_{ads}$ radicals with molecules in the gas phase, particularly methane, can also be a source of acetylene formation *via* the following scheme:

$$^{\bullet}OH + 2C_S \longrightarrow (CO)_{ads} + CH_{ads}$$
$$CH_4 + (CH)_{ads} \longrightarrow (C_2H_5)_{ads} \longrightarrow (C_2H_4)_{ads} + H$$
$$(C_2H_4)_{ads} \longrightarrow C_2H_2 + H_2$$

Summary

In summary, we have shown that hydroxyl radical can react directly with a carbon surface in the range of 200 to 500 °C to produce readily observable quantities of olefins and acetylenes *via* plausible reaction pathways. This finding is significant from an environmental perspective in that this formation is observed in the same temperature range as that reported for formation of PCDD/F and other pollutants in various combustion systems.[41] Olefins and acetylenes are known to undergo polymerization and other molecular growth reactions to form butadiene, aromatics, and PAHs as well as possibly participate in pathways of formation of PCDD/F through surface catalyzed chlorination and molecular growth.[1–5,12,14,15] It should also be noted that in combustion systems that contain large quantities of chlorine,[42] reactive chlorine atoms may play an active role in carbon gasification and formation of CHCs and dioxin precursors. The reactions of combustion-generated radicals with carbon and their role in cool-zone formation of toxic and hazardous air pollutants are the subject of on-going investigations that will be reported in future publications.

Acknowledgements

This research is partially supported by the US Environmental Protection Agency under Grant R626166 and the Patrick F. Taylor Chair Foundation. We gratefully acknowledge Dr Rafael Cueto for kindly supporting several analytical methods used in this work and Daniel Southam, a participant in a summer REU Program (sponsored by NSF), who assisted in a portion of this work.

References

1 F. W. Karasek and L. C. Dickson, *Science*, 1987, **237**, 754.
2 L. C. Dickson, D. Lenoir and O. Hutzinger, *Environ. Sci. Technol.*, 1992, **26**, 1822.
3 R. Addink and K. Olie, *Environ. Sci. Technol.*, 1995, **29**, 1425.
4 M. S. Milligan and E. R. Altwicker, *Environ. Sci. Technol.*, 1996, **30**, 225.
5 S. S. Sidhu, L. Maqsud, B. Dellinger and G. Mascolo, *Combust. Flame*, 1996, **100**, 11.
6 R. Weber and H. Hagenmaier, *Organohalogen Compd.*, 1997, **31**, 480.
7 B. Dellinger and P. H. Taylor, *Cent. Eur. J. Public Health*, 1998, **6**, 79.
8 I. Fangmark, B. Stomberg, N. Berge and C. Rappe, *Environ. Sci. Technol.*, 1994, **28**, 624.
9 H. Vogg and L. Stieglitz, *Chemosphere*, 1986, **15**, 1373.
10 L. Stieglitz, H. Vogg, G. Zwick, J. Beck and H. Bautz, *Chemosphere*, 1991, **23**, 1255–1264.
11 M. S. Milligan and E. R. Altwicker, *Environ. Sci. Technol.*, 1995, **29**, 1353.
12 P. H. Taylor, S. S. Sidhu, W. A. Rubey, B. Dellinger, A. Wehrmeier, D. Lemoir and K.-W. Schramm, presented at *27th Symposium (International)/The Combustion Institute*, The Combustion Institute, Pittsburgh, PA, 1998, p. 1769.
13 L. Khachatryan and B. Dellinger, presented at *7th International Congress on Combustion by Products: Origins, Fate, and Health Effects*, North Carolina, 2001, p. 47.
14 K. L. Froese and O. Hutzinger, *Environ. Sci. Technol.*, 1996, **30**, 998, 1009.
15 K. L. Froese and O. Hutzinger, *Environ. Sci. Technol.*, 1997, **31**, 542.
16 *Soot in Combustion systems*, Ed. J. Lahaye and G. Prado, Plenum Press, New York, 1983.
17 P. H. Taylor, J. A. D'angelo, M. C. Martin, J. H. Kasner and B. Dellinger, *Int. J. Chem. Kinet.*, 1989, **21**, 829.
18 E. Papirer, E. Guyon and N. Perol, *Carbon*, 1978, **16**, 133.
19 C. W. Zielke and E. Gorin, *Ind. Eng. Chem.*, 1955, **47**, 820.
20 H. Imai, S. Nomura and Y. Sasaki, *Carbon*, 1975, **13**, 333.
21 P. Salatino and L. Massimilla, *Chem. Eng. Sci.*, 1989, **44**, 1091.
22 H. Marsh and A. D. Foord, *Carbon*, 1973, **11**, 421.
23 X. Chu and L. D. Schmidt, *Carbon*, 1991, **29**, 8, 1251.
24 S. G. Chen and R. T. Yang, *Energy Fuels*, 1997, **11**, 421.
25 N. Chen and R. T. Yang, *J. Phys. Chem. A.*, 1998, **102**, 6348.
26 Z. H. Zhu, G. Q. Lu and R. T. Yang, *J. Catal.*, 2000, **192**, 77.
27 D. M. Bibby, in *Chemistry and Physics of Carbon*, Ed. P. A. Thrower, Marcel Dekker, New York, 1982, vol. 18, p. 71.
28 J. M. Thomas, in *Chemistry and Physics of Carbon*, Ed. P. L. Walker, Marcel Dekker, New York, 1965, vol. 1, p. 121.
29 *Radicals on Surfaces*, Ed. A. Lund and C. J. Rhodes, Kluwer Academic Publishers, 1995, p. 55.
30 P. Pereira, R. Csencsits, G. A. Somorjai and H. Heinemann, *J. Catal.*, 1990, **123**, 463.
31 L. Stieglitz, *Environ. Eng. Sci.*, 1998, **15**, 5.
32 M. Lasagni, E. Collina, M. Tettamanti and D. Pitea, *Environ. Sci. Technol.*, 2000, **34**, 130.
33 H. Marsh, T. E. O'Hair and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 1965, **61**, 274, 285.
34 B. J. Wood and H. Wise, *J. Phys. Chem.*, 1969, **73**, 1348.
35 M. Balooch and D. R. Olander, *J. Chem. Phys.*, 1975, **63**, 4772.
36 K. G. Neoh, J. B. Howard and A. F. Sarofim, Soot oxidation in Flames, in *Particulate Carbon Formation During Combustion*, Plenum Press, New York, 1981, pp. 261–282.
37 A. Kazakov, H. Wang and M. Frenklach, *Combust. Flame*, 1995, **100**, 111.
38 J. Appel, H. Bockhorn and M. Frenklach, *Combust. Flame*, 2000, **121**, 122.
39 M. S. Akhter, A. R. Choghtal and D. M. Smith, *Carbon*, 1985, **29**, 593.
40 P. Breisacher and P. C. Marx, *J. Am. Chem. Soc.*, 1963, **85**, 3618.
41 G. Schwarz, L. Stieglitz and W. Roth, *Organohalogen Compd.*, 1990, **3**, 169.
42 C. Procaccini, J. W. Bozzelli, J. P. Longwell, K. A. Smith and A. F. Sarofim, *Environ. Sci. Technol.*, 2000, **34**, 4565.