Screening approaches for gas-phase activity of flame retardants

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Abstract

Molecular beam mass spectrometry (MBMS) and optical diagnostic techniques, two common combustion science diagnostic tools for studying the impact of material on flames, are evaluated as tools for estimating the gas-phase potential of polymer-flame retardant additives. The gas-phase activity of hexabromocyclododecane (HBCD), a widely used commercial flame retardant, was studied and compared via the two combustion diagnostic techniques. MBMS data for HBCD were reviewed and provided identification of gas-phase active species as well as quantitative information on the degree of effectiveness based upon reduction of OH in a premixed CH_4/air/N_2 flame. In contrast, optical chemiluminescence detection of OH^* and CH^* provided a simpler technique for monitoring the gas-phase potential of flame retardants. Studies of CH^* and OH^* levels after addition of pyrolyzed products from polystyrene/HBCD blends into a diffusion flame system are compared with MBMS experiments of flames doped with pure HBCD. Comparison of chemiluminescence data with similar data from a small-scale heat release test, the pyrolysis combustion flow calorimeter, indicated that CH^* and OH^* activity relate to the heat release rate for flaming combustion.
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1. Introduction

Many plastic materials are inherently flammable in the pure form. In order to use these plastic materials in certain commercial areas (buildings, vehicles, electronic appliances, etc...), these materials must meet fire safety requirements and must pass certain regulatory fire performance tests [1]. Flame retardant (FR) additives are typically blended with polymers to provide improved fire resistance for many commercial applications. The mechanistic action of FRs can be classified in the general categories of either gas or condensed-phase activity. The principle gas-phase mechanism utilized by many FRs involves chemical inhibition via radical scavenging of key combustion radicals (OH, H, O) to effectively shut down the combustion process. Condensed-phase activity involves action in the solid or melt phase of the polymer to impact/reduce the burning process. An example of condensed activity is the formation of a char layer that can insulate or isolate

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the remaining bulk material from the combustion process. Bromine based FRs are the most widely used FRs in commercial applications for a variety of polymer systems and provide a high level of gas-phase activity through radical scavenging by HBr, formed from the degradation of the parent FR [2]. Environmental scrutiny for many halogen FR systems has led to efforts to identify alternative halogen-free FR systems suitable for commercial polymer applications.

Previous work on mechanistic studies of flame retardant activity has focused on the use of traditional analytical pyrolysis and evolved-gas techniques [3–6]. These methods are limited to the detection of relatively stable degradation species and are unsuitable for detection of unstable radicals and other species. These species are key to the complete understanding of the active flame retardant mechanism. Combustion science diagnostic tools such as molecular beam mass spectrometry (MBMS) and optical diagnostic techniques have been utilized for fundamental studies in combustion science chemistry for many years. These techniques provide the analysis capability to study chemical inhibition and other combustion reactions directly in stable flame systems. In particular, these techniques allow analysis of unstable radical species that are a key part of combustion chemistry.

A few previous studies showed the utility of combustion diagnostic techniques for studying the combustion chemistry of flame retardant additives in flames. Studies by Cullum [7,8] and Siow [9] dealt with the use of laser-induced fluorescence (LIF) to study FR effectiveness by measuring the OH radical response after addition of FR or an FR/polymer blend to a flame system. MBMS was used to look at the combustion chemistry associated with bromine and phosphorous flame retardants [10,11].

In the present work, we review two techniques for assessing the potential gas-phase activity of flame retardants applied to polymer systems: MBMS and optical detection via chemiluminescence. The two techniques are reviewed as potential methods to screen FR candidates for application in polymer systems. The gas-phase activity of hexabromocyclododecane ($C_{12}H_{18}Br_6$), HBCD, a widely used commercial flame retardant, was studied and compared via the two combustion diagnostic techniques.

Previous work with MBMS showed the potential utility of this technique to assess the gas-phase combustion chemistry of flame retardants which included quantitative measurements of FR gas-phase effectiveness based on OH radical depletion measurements [11]. In contrast to MBMS, optical detection by chemiluminescence is presented as an alternative approach that is less complex and can be based on relatively simple instrumentation.

To implement a system based on optical detection of radicals in a flame, a system was implemented based on a pyrolysis heating device that allowed controlled heating of the sample. The off-gases of the pyrolysis were then transferred via a heated transfer-line into a stable flame system with associated optical detection. The optical measurement system monitored the time-dependent response of a flame after the addition of an FR or an FR blend of polystyrene (via the pyrolysis). The prototype system utilized a thermogravimetric analysis for the pyrolysis step. A similar pyrolysis and sample transfer configuration was utilized in the original pyrolysis combustion flow calorimetry (PCFC) instrument developed by Walters and Lyon [12] which has since been improved with a standalone system with a pyrolysis furnace [13]. The PCFC is a small-scale polymer flammability test that measures the heat release rate via forced combustion of polymers after pyrolysis.

For optical detection in the flame, the use of a laser-induced fluorescence (LIF) measurement setup to measure OH radicals was found in preliminary experiments to be not feasible for the transient experiments due to the limited repetition rate of typical LIF systems (10–20 Hz) that did not allow averaging of a significant number of signals to achieve a signal/noise ratio good enough to detect small changes (~10%) in OH concentration. However, recently high repetition rate LIF systems were developed for gas-phase measurements of biacetyl [14] and progress is expected in this field in the future. At this time, chemiluminescence detection was considered to perform time-resolved measurements. The detection of chemiluminescence signals is simple and can be accomplished with high temporal and spectral resolution. It has to be emphasized, however, that the signals that originate from chemically excited species, like OH^* and CH^* are not related to the concentration of ground state OH and CH but both signals have been linked with heat release and hence the strength of a flame [15,16]. Therefore, the chemiluminescence signals from OH^* and CH^* are an attractive target to investigate the impact of FR on flames. The intention is to evaluate whether or not there is a correlation between the amount of FR that is added to a non-premixed flame and the recorded chemiluminescence signal. Such a relation could then also be explored to rank FR compounds in their effectiveness to suppress combustion via gas-phase FR activity. In addition, preliminary data for CH^* and OH^* flame measurements of pyrolyzed samples of HBCD/polystyrene blends are compared with similar measurements with a PCFC instrument. This comparison shows that the CH and OH measurements do track the relative heat release rate for HBCD/polystyrene blends from the PCFC heat release rate testing. The data also

allow comparison between small-scale combustion testing based on flaming versus forced combustion (PCFC).

Both MBMS and optical chemiluminescence techniques are reviewed as potential screening tools to quickly assess the potential of a FR candidate for gas-phase FR activity. MBMS analysis provided a very complete qualitative and semi-quantitative analysis of the gas-phase combustion chemistry after addition of pure HBCD to a flame system. Although the MBMS technique provided a near complete analysis of the gas-phase flame chemistry associated with the FR HBCD, the technique is quite complex and not suitable for routine and rapid screening of FRs in a typical research and development laboratory. In contrast to MBMS, chemiluminescence detection provided limited information but appeared to be better suited as potential screening tool for gas-phase activity of FRs as it is simpler and requires instrumentation that is less complex.
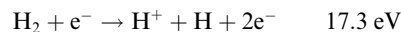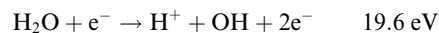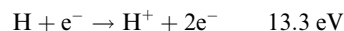
2. Experimental techniques

2.1. Molecular beam mass spectrometry

MBMS studies and instrumentation have been described previously [11]. For flame testing of fire retardants, a premixed $CH_4/O_2/N_2$ (9.18/15.54/75.28, $\phi = 1.18$) flame stabilized on Mache–Hebra nozzle burner [17] was utilized at atmospheric pressure and at initial temperature of the combustible mixture of 368 K. The Mach–Hebra burner used a quartz tube, tapered at one end that results in a uniform distribution of flow velocity over the cross section of the burner outlet. The flame forms a regular cone. A detailed description of the burner and the original system for feeding of solid fire retardants into unburnt gases is described elsewhere [11]. The flow rate of the combustible mixture was varied from 1.5 to 2.16 slpm to keep the height of the flame cone at about 10 mm. HBCD was added to the combustible mixture at loading of 0.018% by volume as vapors.

A flame-sampling molecular beam mass spectrometer employing tunable soft ionization by electron-impact is used for these studies [18]. Detailed descriptions of the instrument and experimental procedures are given elsewhere [11]. This instrument consists of an atmospheric-pressure flame chamber, a differentially pumped molecular beam flame-sampling system, and a quadrupole mass spectrometer. For the current experiments, the geometry of the sampling system was as follows: probe–skimmer distance, 20 mm; probe–collimator distance, 320 mm; probe–ion source distance, 390 mm. Stage 1 was pumped by an oil diffusion pump (2000 L/s), which provided a working pressure of $4–7 \times 10^{-2}$ Pa, while a 0.08-mm orifice probe was used for sampling from a

flame at atmospheric-pressure. Stages 2 and 3 were pumped with two separate turbomolecular pumps (each 500 L/s), which maintained pressures of about 10^{-3} Pa (stage 2) and $2–4 \times 10^{-6}$ Pa (stage 3) during the experiments.

The MS 7302 quadrupole mass spectrometer (Experimental Plant of the Russian Academy of Sciences) was equipped with a modernized ion source with a small spread of electron energy, corresponding only to the thermal spread [19]. A small spread of energy of ionizing electrons permits identification of species with adiabatic ionization energies (IEs) differing slightly from ionization thresholds of fragmentary ions at the same m/z, i.e. operating at low IEs close to the ionization potentials of ambiguous species—atoms, radicals, and unstable molecules. An example of the soft ionization procedures is as follows. The H^+ ion can be formed in at least three ion-molecule reactions in the ion source chamber; ionization of hydrocarbons can also produce H^+. Energies required for these reactions are given below.

$$H + e^- \rightarrow H^+ + 2e^- \qquad 13.3 \text{ eV}$$
$$H_2O + e^- \rightarrow H^+ + OH + 2e^- \qquad 19.6 \text{ eV}$$
$$H_2 + e^- \rightarrow H^+ + H + 2e^- \qquad 17.3 \text{ eV}$$

Similarly OH^+ is formed in at least two reactions in electron-impact ionization:

$$OH + e^- \rightarrow OH^+ + 2e^- \qquad 10.5 \text{ eV}$$
$$H_2O + e^- \rightarrow OH^+ + O + 2e^- \qquad 18.3 \text{ eV}$$
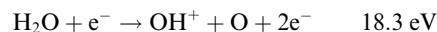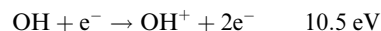
Avoiding the formation of fragmentary ions H^+ and OH^+ from water and H_2 for accurate measurements of the concentration of H atom and OH in a flame requires keeping the IE value between 13.3 and 17.3 eV and 10.5 and 18.3, respectively. A value of 16.2 eV was chosen for this study.

2.2. Flame temperature measurements

Temperatures in the Mach–Hebra flame were measured with a platinum/platinum-10% rhodium thermocouple with SiO_2 anti-catalytic protective coating. The total diameter of the thermocouple with the coating did not exceed 0.030 mm. For measurements in the perturbed (by the probe) flame, the thermocouple was placed at a distance of 0.25 mm from the tip of the probe. Radiative heat losses of the thermocouple were taken into account. More details of thermocouple technique and design of the thermocouple unit are given elsewhere [18].

2.3. Chemiluminescence measurements

A pyrolysis system for controlled heating of the samples (TA Instruments TGA 2950 thermo-

gravimetric analyzer (TGA)) was used to prepare the samples (1–9.1 mg) for introduction into a small methane/air diffusion flame. Methane (50 sccm) and air (600 sccm) flows were set with mass flow controllers (MKS). The flame was protected from surrounding air flow by a quartz tube (dia. 8 mm, height 50 mm). An R-type thermocouple was mounted vertically 5 mm above the visible flame tip within the quartz tube. The temperature of the TGA was increased at a controlled rate (10–60 °C/min) and off-gases passed into the burner via the heated transfer-line (200–250 °C) while at the same time the remaining mass in the TGA was recorded as a function of time. Helium at 80 sccm was used as a carrier for the samples. The flame was 10 mm high and chemiluminescence emissions from the entire flame could be collected through a short focal length lens directly mounted to a fiber bundle that delivered the light to a spectrometer (Newport 77480). A 300 l/mm UV-enhanced grating was chosen to disperse the signal. In combination with a CCD camera (LaVision, ImagerIntense) an external image intensifier (LaVision, IRO) was used as this allowed recording of spectra from 295 to 610 nm. The image frequency was set to 15 Hz. TGA operation was synchronized to the camera software to ensure that the heating temperature ramp and the time-dependent sample mass data were linked to the chemiluminescence signals. The thermocouple signal recording was also linked to the image acquisition. A general schematic is shown in Fig. 1. An example of the time-dependent signals obtained from the chemiluminescence sensor, the thermocouple, and the TGA scale is shown in Fig. 2.

2.4. Pyrolysis combustion flow calorimetry measurements

The PCFC apparatus was constructed by Trace Technologies LLC and is similar in design to the instrument described elsewhere [20]. The heating rate was 1 °C s^{-1}, the maximum pyrolysis temperature was 550 °C and the combustion temperature was 900 °C. The flow was a mixture of O_2/N_2 20/80 cm^3 min^{-1} and the sample weight was $1–10 \pm 0.5$ mg. Each measurement was performed at least twice and the results were averaged.
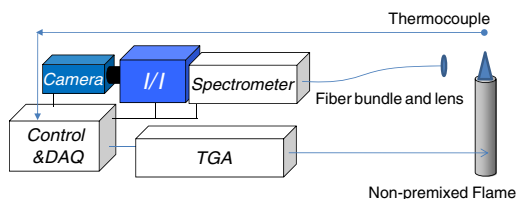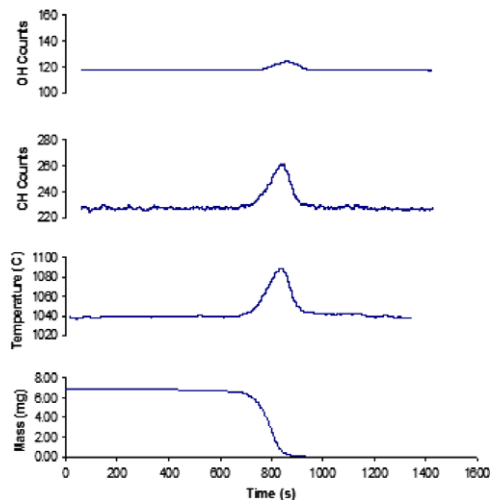

Fig. 2. Changes in signal intensity and temperature above the flame tip are associated with the measured mass loss in the TGA. Note that the increase in chemiluminescence intensity and temperature is a result of the fuel contents of the polymer blend that is added to the flame.

3. Results and discussion

3.1. Review of molecular beam mass spectrometry measurements

MBMS measurements for HBCD have been described previously [11]. Figure 3 gives temperature profiles in the flame without additives and doped with 180 ± 10 ppm of HBCD. The post-flame temperature of the undoped flame was 1966 K, those of HBCD-doped were 1856 K to give an overall change of 110 K and an increase in the width of the combustion zone by a factor of ~1.6–1.7. The calculated temperature profile
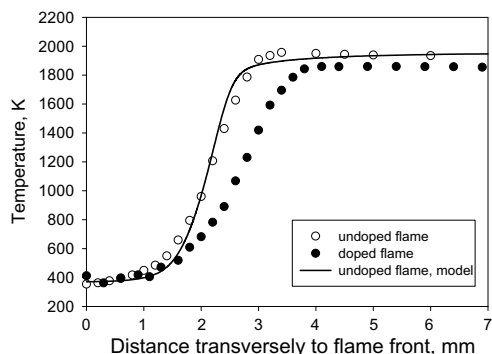

Fig. 1. General schematic of pyrolysis burner system and chemiluminescence setup used in flame studies.

Fig. 3. Temperature profiles in CH$_4$/O$_2$/N$_2$ flame without additive (open symbol – experiment, line-modeling) and doped with 180 ppm of hexabromocyclododecane (filled symbols).

for the undoped flame in Fig. 3 is in good agreement with the measured profile. Calculations show that when methane is added to a combustible mixture in a small amount the expected change in the final temperature is only ∼20 K (based on the total carbon and hydrogen content in the retardant molecule). This confirms that the change in temperature after addition of HBCD comes from the thermal perturbations by the probe and the change in the width of the combustion zone.

Key bromine-containing (HBr, Br) degradation species from HBCD-doped flames were identified and are shown in Fig. 4. HBr and Br represent key species in the scavenging of combustion radicals [21].

Figure 5 gives the OH concentration profile in the flame without HBCD additive and doped with HBCD. From the OH concentration profile, the HBCD additive reduced both the maximum and final concentrations of OH by about a factor of ∼1.1–1.3. Similar OH data as well H data were reviewed recently [11] and confirm that the changes are mainly kinetic as opposed to a thermal effect from the flame temperature changes. The decrease in OH is due to the reactions of HBr with OH, which is well known as a key gas-phase reaction for HBr (HBr + OH → Br + H_2O).

Flame velocity was estimated by the change in flame cone height before and after addition of flame retardant. Details are described elsewhere [11]. According to the measurements, the burning velocity of the undoped flame was 23.5 ± 1.1 cm/s and those of HBCD-doped flames were 19.7 ± 1.2 cm/s. The addition of 180 ppm (by volume) HBCD decreased the burning velocity by about 16% and very close to the drop in OH measured via the MBMS measurements, which confirms the utility of the MBMS technique.
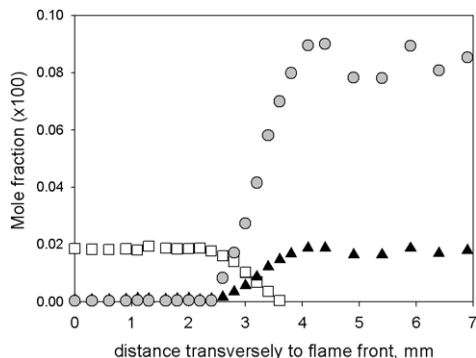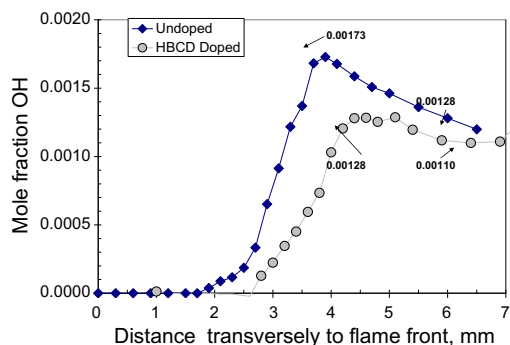

Fig. 5. Profile of OH concentration in $CH_4/O_2/N_2$ flame with and without added HBCD at 180 ppm.

3.2. Chemiluminescence measurements

The entire emission spectrum was recorded at a rate of 15 Hz for the duration of each pyrolysis test, typically about 20 min. From such sequences of spectra species-specific time-resolved information can be extracted by integrating the chemiluminescence signals within a set bandpass, i. e. 300-330 nm for OH* emissions. The mass-loss trace from the TGA was used to determine the flow rate of FR into the flame. Average FR fractions were up to 0.004% (0.008% peak) based on the total volume flow rate of all gases and if referenced to the methane flow only, the fraction was not higher than 0.05%.

The polymer/FR blends themselves contain a significant amount of fuel so that the non-premixed flame actually exhibits a visible burst in intensity and growth in flame height during the main mass loss recorded by the TGA system. Referenced to the methane mass flow rate, the polymer blend added no more than 1% fuel (by mass) to the flame. This is reflected in an increase in OH*, CH* intensity, and temperature from their steady-state values before the FR blend was added. A detailed analysis of a large number of samples with varying overall sample mass as well as different FR fraction in the blends shows that for a fixed FR fraction blend the increase in temperature, OH*, and CH* intensity is proportional to the mass of added polymer blend (see Fig. 6 for an example) for the range of added polymer/FR mass in this study. The CH* intensity exhibits the highest sensitivity of the three signals (CH*, OH*, temperature) to the mass of polymer blend added. It is also evident from Fig. 6 that the increase of measured intensity is lower with increasing fraction of FR in the blend. This is expected for two reasons. First, polymer (=fuel) is substituted for FR so less additional fuel is available. Second, the added FR suppresses combustion. To isolate the net impact of the FR, the chemiluminescence signals are processed as follows.
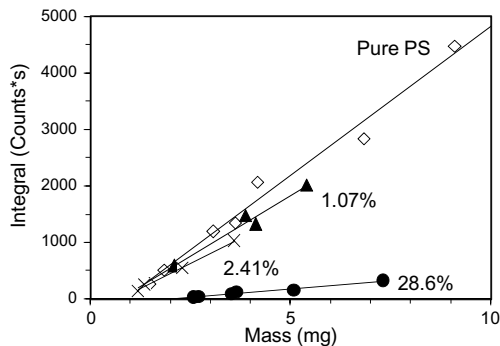

Fig. 4. Concentration profiles of bromine-containing compounds in $CH_4/O_2/N_2$ flame doped with 0.018% of HBCD.

Fig. 6. The measured integrated signal intensity of CH* from the entire flame increases linearly with the amount of polymer/FR blend that is added to the flame. The percentages given are the mass fraction of HBCD that is included in the blends. Note that the net change of measured intensity is positive due to the fuel contents of the blends.

For the unperturbed flame, the signal intensity is steady at

$$I_{CH^*} = \text{constant} \tag{1}$$

For a given mass m of pure polymer that is added to the flame, the integrated chemiluminescence intensity is modified to

$$I_{CH^*} = \text{constant} + m_{PS} \left(\frac{dI_{CH^*}}{dm_{PS}} \right) \tag{2}$$

The expected signal $I_{CH^*}(m_{PS\ in\ blend})$ from the polymer fraction in a blend can then therefore be calculated by using Eq. 2 and the net mass of pure polymer. It is found, that the measured intensity is always below the expected value, indicating a flame weakening due to the FR. The fractional change Δ in measured intensity is then defined to produce an absolute measure of the impact of the FR on chemiluminescence. Notice also that here the steady-state intensity has been removed. A precision error of approximately 4% for Δ was determined using the calculated slopes in Fig. 6.

$$\Delta = \frac{I_{CH^*}(m_{PS\ in\ blend}) - I_{CH^*}(m_{Blend})}{I_{CH^*}(m_{PS\ in\ blend})} \tag{3}$$

The data shown in Fig. 7 indicate that the use of CH* signals would provide the highest sensitivity with respect to the amount of FR added to the flame. The chemiluminescence detection is set up to collect emissions from the entire flame and therefore provides a measure of the overall impact of FR addition to the flame. In contrast to that, the temperature measurement with the thermocouple is performed at one location, a few millimeters above the visible tip of the unperturbed flame. Once the pyrolysis products enter the flame, the flame height increases and thus the ther-
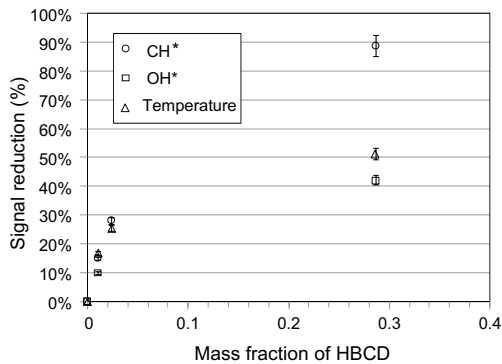

Fig. 7. The mass-normalized reduction of signal intensity is most sensitive for CH*. OH* and temperature exhibit similar reduction for a given amount of HBCD.

mocouple is exposed to a hotter region of the flame. Adding more FR to the blend will produce less of a gain in flame height and the measured temperature increase is lower. With this, the measurement of the effectiveness of a FR substance will critically depend on the exact alignment of the thermocouple with respect to the flame tip and to flame flow settings. It is expected that an integral measurement such as the chemiluminescence measurement is much more immune towards details of the operating conditions.

It also has to be mentioned that chemiluminescence signals are susceptible to quenching just as excited molecules are in LIF experiments. For fully quantitative analysis of FR activity when examining different molecule classes it might therefore be necessary to address luminescence quenching. A Stern–Vollmer analysis of the present data shows a non-linear Stern–Vollmer behavior, suggesting that the measured reduction in signal is not simply the result of quenching but does reflect the impact of the FR activity.

3.3. Preliminary comparison between chemiluminescence and pyrolysis combustion flow calorimetry results

PCFC data were collected for the same set of samples listed in Fig. 6. PCFC is a heat release measurement method based on forced combustion of the volatile pyrolysis components [13]. A comparison of these parameters with chemiluminescence signals should allow confirmation that CH* and OH* do track the heat release from flaming combustion. A key PCFC data point is the heat release capacity (HRC). HRC values are representative of the overall heat release potential for a material and is taken from the peak HRR divided by the scan rate. Similar data (peak measurements) were generated for chemiluminescence data and a correlation plot is shown in Fig. 8. The peak chemiluminescence data (peak CH or OH
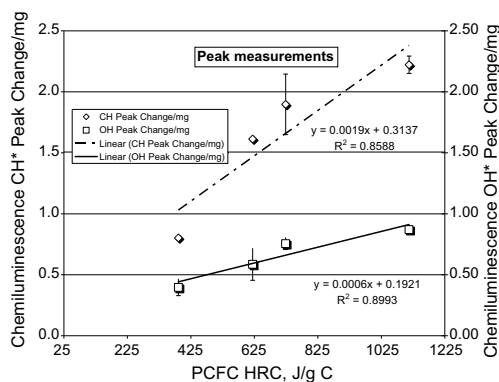
Fig. 8. Comparison between integral and peak measurements from chemiluminescence and PCFC.

signal/mass) show a reasonable linear correlation with the corresponding PCFC peak data, HRC. The data seem agree with the proposal that CH* and OH* chemiluminescence signals represent the heat release for flaming combustion [15]. More research is needed but the preliminary data show a general correlation between HRR for flaming combustion and forced combustion.

3.4. Comparison of MBMS and chemiluminescence results

A 24% decrease in OH concentration in a rich premixed methane/air flame after the addition of 180 ppm HBCD was measured with MBMS. Additionally, the impact of HBCD addition on the flame structure is resolved in the spatial concentration profile. The delay in the OH concentration and temperature drop in the presence of the FR indicate a decrease in flame speed. Such information cannot be obtained from the integral chemiluminescence measurements. The overall impact on heat release is indirectly determined via the measurement of OH* and CH* light intensity. In the non-premixed methane/air flame that was investigated here, the addition of 37 ppm HBCD led to a reduction of the space- and time-integrated CH* signal of 89% and a reduction of the OH* signal by 42%. Thus, the chemiluminescence measurements appear to show more sensitivity in terms of signal reduction for given amount of FR addition. One clear difference in the two methods lies in FR/fuel type used in the combustion studies. MBMS relies on a major simplification by elimination of the polymer and instead uses a fuel-rich flame to duplicate polymer combustion. Such an assumption neglects any potential polymer-FR interactions. In contrast, the presented studies for chemiluminescence measurements utilize pyrolysis of polymer/FR blends for flaming combustion measurements and thus polymer-FR interaction are possible.

4. Conclusions

Investigations on how to assess the activity level of flame retardants were performed in premixed and non-premixed flames. HBCD and its mixtures with polystyrene were used as an example substance class. The impact of the FR addition on OH radical concentrations and temperature profiles could be measured in a slightly rich premixed methane/air flame using a molecular beam mass spectrometry. Information obtained this way is very important for validation and development of detailed chemical kinetic mechanisms. Furthermore, OH radical concentration changes can be interpreted as a quantitative measure of the effectiveness of a FR. However, for routine testing during the development of new FR molecules the use of an MBMS system is too expensive and time-consuming. The present work demonstrated that time-resolved but space-integrated chemiluminescence measurements of CH* and OH* emissions can be used to quantify the impact of FR addition to a flame. In a non-premixed methane/air flame the sensitivity to FR addition was about five times higher compared to FR addition to premixed rich methane/air flames and quantitative OH radical concentration measurements using MBMS. Thus, although the chemiluminescence measurements don't provide the all of combustion chemistry diagnostic capabilities, it is more suitable as a potential FR screen for gas-phase activity.

Acknowledgments

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