In-Situ Characterization of Flame Retardant Polymer Systems Using Laser Spectroscopic Methods

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Research Objective: To develop and test new spectroscopic methods that can be used to investigate, in-situ, the affects of flame retarding chemicals on combustion in real-world types of systems. Emphasis is on qualitative tests that can be used in “dirty,” or non-ideal flame environments. And, to test these techniques on new types of flame retarding chemicals.

Approach: The approach that we have taken is to investigate steady-state and time-resolved laser-induced fluorescence methods tomeasure chemical effects in simple, “dirty,” combustion systems such as a methane/air flame. Emphasis is on the use of combustion systems that are not “idealized” but that can be used with complex flame retarding mixtures. The combustion process itslef is not the primary focus, rather we make measurements that can be related to the potential effectiveness of flame retarding chemicals. For example, for some brominated flame retardants, the effect on the fluorescence lifetime of OH radicals seems to be related to its effectiveness as a combustion inhibitor in certain types of polymer blends.

Accomplishment Description:

- Developed a new method based on time-resolved (TR) laser-induced fluorescence (LIF) of hydroxyl radicals to qualitatively compare certain types of flame retardant systems and to quantitatively compare the efficiency of certain new brominated flame retardants.

- Used LIF and TRLIF to follow the dynamics of two common brominated flame retardants and two similar model bromine compounds, in a simple methane flame (e.g., “dirty” flame).

- Developed a novel dual-laser-pulse lifetime imaging (DPLI) method that can be generally applied to combustion and flame studies. The new technique allows picosecond lifetimes to be measured in a flame environment using simple instrumentation.

- Submitted a paper to *Appied Spectroscopy* describing a new type of time-resolved imaging technique that resulted from this work.

- Disclosed patents on the TRLIF and DPLI methods.

- Developed a method to reproducably injecting insoluble plaques into a flame using laser ablation.

• Leveraged funding (~$127K) from Albemarle Corporation to apply the TRLIF method for new types of nonbrominated flame retardants (Note: this is independent of funds obtained by Tour's group from Albemarle Corporation).

Laser induced fluorescence (LIF) has been used to follow brominated flame retardant reactions in a simple methane/air flame by directly adding known concentrations of flame retardant compounds to a methane/air flame. Through the use of OH radical time-resolved LIF in the flame, it was possible to quantify the relative efficiency of selected flame retardants (Figure 2). Similar non-flame retarding brominated compounds did not show this effect on the OH radical fluorescence intensity when aspirated into a flame with the appropriate polymer. The TRLIF method is based on the fact that the flame inhibition mechanism for certain types of flame retarding (FR) chemicals, such as brominated FRs, is by dynamic quenching of the OH radical. While for other types of FR chemicals, flame inhibition is the result of physical effect. Figure 2 shows that upon addition of increasing concentrations of a brominated flame retardant, HBCD, the OH radical fluorescence lifetime decreases dramatically—a direct result of the known dynamic quenching mechanism. However, when a structurally similar compound (cyclohexyl bromide) is added, the OH radical fluorescence lifetime increases, probably as a result of flame cooling—a physical mechanism. In future work we would like to determine if this technique can be used to quantitatively screen other halogenated and non-halogenated flame retardants. A novel dual pulse fluorescence lifetime imaging (DPLI) technique was developed that uses very simple instrumentation to measure picosecond fluorescence lifetimes. In this technique a pulsed laser is used with an inexpensive non-gated charge coupled device (CCD) camera. Two laser pulses are applied with at least one of sufficient power to saturate fluorescence in the system. By obtaining images with various time delays between laser pulses, it is possible to reconstruct a two dimensional fluorescence lifetime image that is capable of picosecond time resolution. Figure 2 shows the use of this technique to study the interface between immiscible solvents.

Significance: The time-resolved LIF techniques we are currently developing might be useful for qualitative screening of certain types of flame retardant systems. For example, we have shown that the these methods can be used to measure the relative ability of selected brominated flame retardants to inhibit combustion in a simple methane flame. If successful, such methods will be useful for quickly screening a large number of prospective flame retardants allowing the most efficient ones to be more quickly identified and brought to market. <u>This will, 1) reduce the costs of these materials thus reducing the costs of their use in aircraft manufacture, and 2) ultimately reduce the risk of combustion related deaths and injuries during aircraft crashes</u>.

Expected Results: The new TRLIF techniques being developed will be useful for rapid qualitative assessment of certain types of flame retardant chemicals. This, in turn, enables effective systems to be more quickly identified and brought to market, thus reducing costs. The DPLI technique we are developing will be much more generally useful for a wide range of combustion studies involving chemical species with very short lifetimes.

References: Larsen, E. R., JFF/Fire Retardant Chemistry**, 1975**, *2*, 5. Butlin, R. N., and Simmons, R. F., Combust. Flame, **1968**, *12*, 447.

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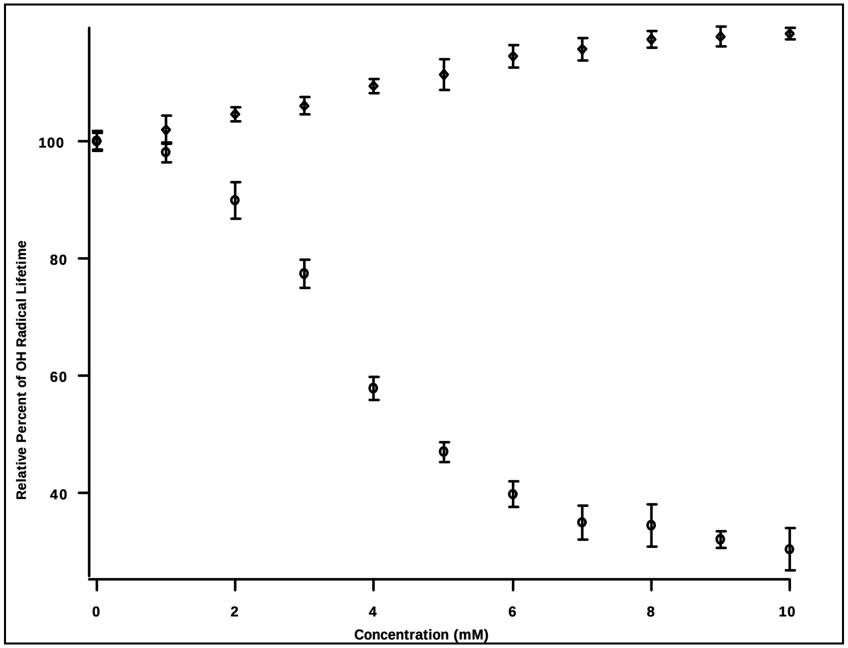

Figure 1 (left). Percent of OH fluorescence lifetime vs concentration for HBCD (open circles) and cyclohexyl bromide (solid diamonds). This plot shows the dramatic effect the known flame retarding chemical, HBCD, has on OH radical lifetime compared to the small, and opposite, affect of a non-flame retardant chemical, cyclohexyl bromide, on the OH radical lifetime.

Figure 2 (right). Lifetime image of the interface between water and methylene chloride using the new DPLI method. The top shows the LIF image of the interfacial region obtained by doping the solvents with a low concentration of rhodamine B. The lower image shows fluorescence lifetime of rhodamine B versus position in the interface region.