

**SPECTRALLY AND TEMPORALLY RESOLVED LASER  
INDUCED FLUORESCENCE (LIF) PROVIDES INSIGHT  
INTO THE MECHANISM OF FLAME RETARDATION**

Brian M. Cullum, Pramod K. Khulbe, Brian J. Marquardt  
and S. Michael Angel\*

*Department of Chemistry and Biochemistry  
University of South Carolina  
Columbia, South Carolina 29208  
Phone (803) 777-2779  
Fax (803) 777-9521  
E-mail : Angel@psc.sc.edu*

*\*-Author to whom correspondence should be sent*

**KEYWORDS:** laser induced fluorescence, brominated flame retardants, and time resolved

**ABSTRACT**

Presently two major theories exist on how flame retardants work.<sup>1,2</sup> Temporally resolved LIF has been used to determine the extent to which the chemical kinetic theory of flame retardation applies to the effect of brominated flame retardants, such as decabromodiphenyl oxide (DECA) and hexabromocyclododecane (HBCD), on flame retardation. We have shown that the primary effect of these brominated flame retardants is chemical in nature as opposed to physical, lending credence to the radical trap theory of flame retardation.

**INTRODUCTION**

In the present work, we are measuring the effect of two brominated flame retardants (HBCD and DECA) on the concentration of OH radicals in a methane/air flame. This is done by monitoring both the laser induced fluorescence (LIF) intensity and the fluorescence lifetime of the  $\cdot\text{OH}$ . In these experiments, we monitor the  $\cdot\text{OH}$  fluorescence intensity and lifetime while aspirating various concentrations of the flame retardants dissolved in toluene into the flame. Monitoring the lifetime of the radical species provides insight into the flame inhibition process because  $\cdot\text{OH}$  is a key species in the propagation of combustion in a flame. If the primary method of inhibition was based on the heat capacity of the brominated species, removing heat from the reaction, then the rate of molecular collisions and temperature in the flame would be reduced. This in turn would cause the fluorescence lifetime of the flame species, including  $\cdot\text{OH}$ , to increase. However, if the primary mechanism of action of these brominated flame retardants is based on the radical trap theory, then the  $\cdot\text{OH}$  radical, and other radical flame species that can be dynamically quenched, would show a reduction in lifetime proportional to the amount of bromine introduced into the flame. In this study we provide evidence that suggests that this is the case. From instantaneous intensity measurements, it can be shown that the concentration of ground state  $\cdot\text{OH}$  is depleted upon addition of brominated flame retardants. In addition  $\cdot\text{OH}$  lifetime measurements show that the  $\cdot\text{OH}$  excited state is also being quenched upon addition of brominated flame retardants, suggesting that the reactivity of the excited state and ground state are similar and that the mechanism of quenching of the ground state is chemical.

**EXPERIMENTAL**

**LIF setup**

In these experiments, a frequency doubled fundamental of a Q-switched Nd:YAG laser (Quantel International Model 580-20) was used to pump a frequency doubled dye laser (Continuum Model Nd6000) using Rhodamine 6G and emitting approximately 3.5 mJ/10 ns pulse at 281.10 nm. The laser wavelength was tuned to the  $A^2\Sigma^+ \rightarrow X^2\Pi$  transition of  $\cdot\text{OH}$ . The laser beam was focused to a point on the front edge of a six inch slot burner using an f/8 plano convex lens. This supplied sufficient laser power to saturate the  $\cdot\text{OH}$  radical in the flame.  $\cdot\text{OH}$  fluorescence was collected by an f/4 lens and focused onto the slit of a 0.85 meter double monochromator (SPEX model 1404), with 0.012 nm resolution, to resolve the 314.58 nm emission. The fluorescence signal was monitored using a photomultiplier tube (Hamamatsu

Model R2949) that was 50  $\Omega$  - coupled to a 500 MHz digital sampling oscilloscope (LeCroy Model 9350L).

In addition to the setup described above, the temperature of the flame was monitored using thermally assisted laser induced fluorescence (TALIF) of  $\cdot\text{OH}$ . This required the laser dye to be changed to Rhodamine 101 and a wavelength of 306.80 nm to be produced. This excitation scheme promotes electrons from the ground vibrational level of the  $X^2\Pi$  state to the ground vibrational level of  $A^2\Sigma^+$  state.

## RESULTS AND DISCUSSION

### $\cdot\text{OH}$ Concentration

By monitoring the change in intensity of the LIF signal at various concentrations of flame retardant it can be seen that increased flame retardant concentrations have a dramatic effect on the  $\cdot\text{OH}$  radical concentration. This is in good agreement with results reported previously by several authors.<sup>1-5</sup> The decrease in LIF shows that the flame retardant is removing  $\cdot\text{OH}$  radicals from the flame. The results show that PVC/HBCD mixtures cause a dramatic reduction in LIF signal with even small amounts of HBCD added. This is in agreement with the theory that one of the primary modes of flame retardation is by removing the highly energetic species of  $\cdot\text{OH}$ , by either preventing formation of the  $\cdot\text{OH}$  or by removing it from subsequent propagation steps. In addition, increased concentrations of DECA with and without 4%  $\text{Sb}_2\text{O}_3$ , were aspirated into the burner to determine their relative affect on  $\cdot\text{OH}$  in the flame. The first observation of this shows that the HIPS/DECA mixtures without  $\text{Sb}_2\text{O}_3$  show little or no change in the relative amount of  $\cdot\text{OH}$  present. Although not well understood, it has been observed that DECA requires the addition of  $\text{Sb}_2\text{O}_3$  as a synergist before it has any noticeable flame retardant properties.<sup>6</sup> In addition to this it can be seen that the relative amount of  $\cdot\text{OH}$  present in the flame is very sensitive to the concentration of DECA added, with 4%  $\text{Sb}_2\text{O}_3$ , and begins to level off at approximately 7-8% (w/w) bromine. This corresponds to the 3:1 stoichiometric ratio of Br to Sb, which has been found to be optimal for this compound.<sup>6</sup> At any point beyond this ratio Sb becomes the limiting reagent in the system, and removal of  $\cdot\text{OH}$  is expected to level off as observed.

### $\cdot\text{OH}$ Lifetimes

Time resolved LIF of  $\cdot\text{OH}$  in the flame front of an atmospheric premixed methane/air flame has been reported to range between several hundred picoseconds up to 8 ns depending on the flame conditions that are used as well as the region of the flame that is probed.<sup>7-19</sup> If reduction of  $\cdot\text{OH}$  concentration in the flame occurs by collisional quenching of the excited state, or dynamic quenching, a reduction in the fluorescence lifetime would occur. However, if the physical model were to be the primary mechanism of inhibition then the temperature of the flame would decrease causing fewer collisions, thereby increasing the lifetime of the  $\cdot\text{OH}$ .

All fluorescence lifetimes are relative to the lifetime of  $\cdot\text{OH}$  with the polymer dissolved in toluene and aspirated into the flame. From this work it is evident that the lifetime of  $\cdot\text{OH}$  significantly decreases upon addition of HBCD, approximately 40% of the original lifetime. This provides evidence to support the idea of dynamic quenching of  $\cdot\text{OH}$ , or the radical trap theory. While it does not prove that  $\cdot\text{Br}$  is the species in the flame responsible for this trapping, it is strong evidence that  $\cdot\text{OH}$  is being actively removed from the system by collisional reactions with some species produced from HBCD. The change in lifetime begins to level off at higher flame retardant concentrations, probably an artifact caused by the  $2.0 \pm 0.1$  ns resolution of the LIF system. In the case of HBCD, the lifetime should continue to decrease up to the point that the probability between the two molecules colliding is virtually zero.

To determine whether this radical trap theory is the primary source of inhibition for the combination of DECA with HIPS, the same experiment was performed. Interestingly, when the relative change in  $\cdot\text{OH}$  lifetime is plotted for the mixture of HIPS with various concentrations of DECA, there is no significant change. However, when those same concentrations of DECA in HIPS are blended with 4%  $\text{Sb}_2\text{O}_3$  and aspirated into the burner, a dramatic decrease in the  $\cdot\text{OH}$  lifetime was observed. At the maximum DECA concentration this lifetime decreases to approximately 55% of the lifetime without flame retardant and synergist. This leads to the idea that the mixture of DECA, HIPS and 4%  $\text{Sb}_2\text{O}_3$  also generates radical traps as did the

HBCD/PVC combination. In addition, it shows that without the synergist this collisional inhibition does not occur. This suggests that the  $\text{Sb}_2\text{O}_3$  is responsible for the dynamic quenching or is necessary for creating species such as  $\text{SbBr}_3$  that may be responsible.<sup>6</sup>

In an attempt to try to model the data from these flame retardants, structurally similar compounds for HBCD and DECA were chosen. These compounds were cyclohexyl bromide and bromobenzene respectively. Each of these compounds were diluted in toluene to concentrations covering the same range as the flame retardants concentrations used. These compounds show an unexpected trend in the  $\cdot\text{OH}$  lifetime. In both cases, the lifetimes increased slightly. In the case of cyclohexyl bromide, the highest concentration yielded a lifetime approximately 116% of the toluene/PVC solution aspirated into the flame. While for bromobenzene this increase in lifetime was approximately 112% of the toluene/HIPS blank. These results lead to the conclusion that these compounds do not dynamically quench  $\cdot\text{OH}$  in the flame. However, the relative  $\cdot\text{OH}$  concentration in the flame does decrease slightly with increasing concentrations of the brominated species. Therefore it would seem that there is a reduction in the combustion due to the presence of these compounds. However, it appears to be physical in nature. Following the heat capacity theory of Larsen one would expect the lifetime of the  $\cdot\text{OH}$  to increase in this case.<sup>2</sup> The addition of heat absorbing species into the flame reduces the temperature and thus the  $\cdot\text{OH}$  concentration. In addition, by removing heat, or energy, from the flame, there will be fewer collisions and the lifetime of flame species such as  $\cdot\text{OH}$  is expected to increase slightly.

#### Temperature Measurements

Flame temperature measurements were made on the flame itself; with polymer added; with polymer and 30% flame retardant; and with polymer, and 30% flame retardant with 4% synergist added. The temperature of the methane/air flame with no added sample was determined to be 1962 K with a standard deviation of 6 K (based on five replicate measurements). The temperature decreased to approximately 1610 K when the polymer alone was aspirated into the flame. This is because the flame was fuel rich to begin with and the addition of toluene as the polymer solvent increased the amount of fuel in the flame without increasing the oxidizer. There was no further change in the flame temperature upon addition of the flame retardants. This lends credence to the thought that the primary mechanism of action of these flame retardants is not physical, or the temperature would have decreased with the addition of flame retardant and synergist.

#### CONCLUSIONS

In the work presented here, we show that the addition of the halogenated flame retardants, HBCD and DECA with 4%  $\text{Sb}_2\text{O}_3$ , to a methane/air flame reduces the amount of  $\cdot\text{OH}$  present thereby inhibiting combustion. More importantly however, is the fact that the chemical kinetic theory of flame retardation by halogenated flame retardants is supported by time resolved LIF. While the physical theory proposed by Larsen<sup>2</sup>, is shown not to be the primary source of inhibition. The results using the compounds cyclohexyl bromide and bromobenzene which were chosen to model HBCD and DECA respectively seem to support the fact that there is a physical flame suppression component, while the overall decrease in  $\cdot\text{OH}$  lifetime for the flame retardants shows that the primary inhibition comes from a chemical quenching mechanism. In addition, this technique appears to be a good means of quantitating the efficiency various brominated flame retardants, and possibly non-brominated flame retardants.

#### ACKNOWLEDGMENTS

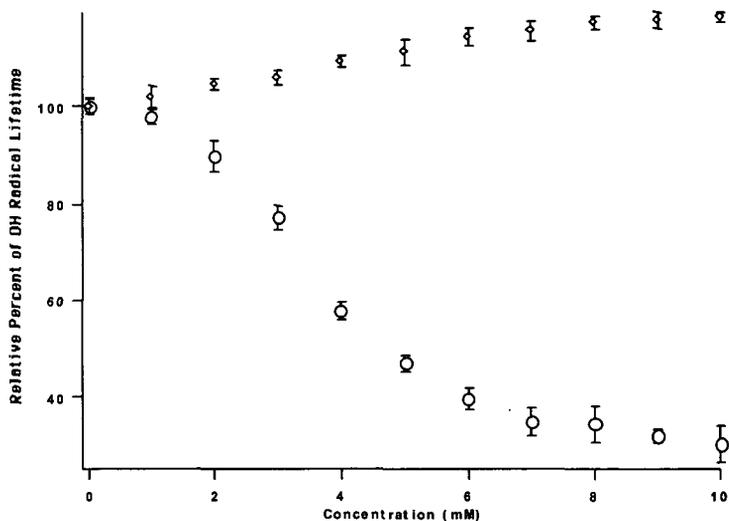
We would like to gratefully acknowledge Dr. Rich Lyon of the Federal Aviation Administration (FAA) for support of this work under grant # 95-G-030. Also, we would like to thank Albemarle Corp. for samples of the flame retardants that were used in this work, and for helpful conversations with Dr. Sam Thomas and Dr. Govind Kumar.

#### REFERENCES

1. Butlin, R. N., and Simmons, R. F., *Combust. Flame* 12:447 (1968).
2. Larsen, E. R., *JFF / Fire Retardant Chemistry* 2:5 (1975).
3. Coward, H. F., and Hartwell, F. J., *J. Chem. Soc.* 1522 (1926).
4. Coward, H. F., and Gleadll, J. J., *J. Chem. Soc.* 243 (1930).
5. Coward, H. F., and Jones, G. W., *Bull. Bur. Mines* 503 (1965).
6. Pettigrew, A. *Encyclopedia of Chemical Technology*. Kirk - Othmer, New York, NY, 1993; p. 954.
7. Köllner, M., and Monkhouse, P., *Appl. Phys. B* 61:499 (1995).
8. Schwarzwald, R., Monkhouse, P., and Wolfram, J., *Chem. Phys. Lett.* 158:65 (1989).

9. Alfano, A., *Appl. Opt.* 28:5010 (1989).
10. Kohse-Höinghaus, K., Jefferies, J. B., Copeland, R. A., Smith, G. P., and Crosley, D. R., *Twenty-Second Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1986, p. 857.
11. Stepowski, D., and Cottreau, M. J., *Combust. Flame* 40:65 (1981).
12. Cattolica, R. J., and Mataga, T. G., *Chem. Phys. Lett.* 182:623 (1991).
13. Heard, D. E., Jeffries, J. B., and Crosley, D. R. *Chem Phys. Lett.* 178:533 (1991).
14. Fiechtner, G. J., King, G. B., Laurendeau, N. M., and Lytle, F. E. *Appl. Opt.* 31:2849 (1992).
15. Garland, N. L., and Crosley, D. R. *Twenty-Second Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1986, p.1693.
16. Smith, G.P., and Crosley, D. R. *J. Chem. Phys.* 85:3896 (1986).
17. Fairchild, P.W., Smith, G. P., and Crosley, D. R. *J. Chem Phys.* 79:1795 (1983).
18. Smyth, K. C., Tjossem, P. J. H., Hamins, A., Hamins, J. H., and Miller, J. H. *Combust. Flame* 79:366 (1988).
19. Andresen, P., Bath, A., Gröger, W., Lülff, H. W., Meijer, J. J., and Meulen, T. *Appl. Opt.* 27:365 (1988).

### FIGURES



**Figure 1:** Relative effect of HBCD (shown by hollow circles) and cyclohexyl bromide ( shown by hollow diamonds) on the fluorescence lifetime of  $\cdot\text{OH}$  radical. The concentrations of these compounds in a toluene solution is shown on the x-axis, and the relative effect of  $\cdot\text{OH}$  radical lifetime is shown on the y-axis. The  $\cdot\text{OH}$  radical lifetime is shown with respect to the lifetime of  $\cdot\text{OH}$  radical when polymer and solvent are aspirated into the burner.