

ANALYSIS OF CF₃Br INHIBITION MECHANISM ON METHANE PREMIXED COMBUSTION

C. Osorio¹, E.L. Petersen² and M.S. Mannan¹

¹Mary Kay O'Connor Process Safety Center, Texas A&M University, USA

²Department of Mechanical Engineering, Texas A&M University, USA

Halon 1301 (CF₃Br) has been widely used for many years due to its high extinguisher efficiency at low concentrations, high dispersion capabilities, and good chemical stability at standard conditions. It represents an ideal fire suppressant for those inhabiting close environments such as aircrafts, ships, oil platforms, etc where evacuation is almost impossible. Despite these advantages, bromo-fluorocarbons are associated with the ozone layer destruction as suggested by Rowland and Molina in 1973. Considering the importance of the stratospheric ozone layer which protects life on Earth from solar radiation, in 1987 the Montreal protocol banned the production of substances with high ozone depletion potential, including Halon 1301. This ban has led to the necessity of finding cleaner alternatives with similar Halon 1301 capabilities; however, no substance has been found to meet such criteria. Progress in this field requires a better understanding of flame inhibition mechanisms, since much of the current knowledge on inhibition is empirical and unclear. Considering this lack of knowledge, the main objective of this work is to obtain further insight into the kinetic effects of CF₃Br as an inhibitor of hydrocarbon combustion, especially methane. Numerical analysis is used to simulate premixed flames using Chemkin[®]. Experimental validation is carried out using a shock tube where premixed combustion is achieved at atmospheric pressure over a range of temperatures using mixtures of methane, oxygen, and an inhibitor highly diluted in argon. Reaction progress is monitored using OH* chemiluminescence at 310 nm, a photomultiplier tube and a narrowband filter. Parameters such as ignition delay times and the resulting OH* time histories are used to compare the results from the experiment with the model predictions. Methane chemistry is based on GRI 3.0, CF₃Br chemistry is from the mechanism of Westbrook (1983), and the OH* chemistry is modeled using the mechanism of Hall and Petersen (2007). The results herein show the chemical mechanism compares well with experiment for ignition times, but some improvement can be made with respect to OH-radical concentration histories.

INTRODUCTION

For many years, Halon 1301 (CF₃Br) has been recognized as an ideal fire suppressant, especially due to its high efficiency on fires caused by flammable liquids and explosive gases. Additionally, this compound presents a high speed of dispersion, leaves no residue that could damage the equipment being protected, is non-corrosive, electrically non-conductive, stable under long-term storage, and it is considered the safest halogenated fire suppressant [1]. Because of all these advantages, Halon 1301 has been widely used by numerous manufacturing, electronic and aviation industries as a fire extinguisher and inerting agent. Particularly, Halon 1301 is considered the best fire extinguisher agent on those closed inhabited environments such as aircrafts, ships and oil platforms, where evacuation is almost impossible [2].

Unfortunately, like chlorofluorocarbons (CFC), Halons present a formidable environmental hazard since they contribute to the depletion of the ozone layer [3]. As suggested by Rowland and Molina, CFC molecules can remain for long terms in the atmosphere until they reach the stratosphere, where they break due to the action of UV light [4]. This event causes a release of active species, such as chlorine, that can rapidly destroy large amounts of stratospheric ozone [4]. It is known that Halons present the same mechanisms as CFC; however, their effect is more significant since bromine species are also involved

[5]. Considering the importance of the ozone layer, which protects life on Earth from solar radiation, the production of substances with high ozone depletion potential has been banned under the International Montreal Protocol in Canada and the national Clear Air Act in the USA [6, 7].

In response to this action, numerous studies have attempted to find a substitute with similar Halon 1301 capabilities. One of the major trends looks for environmentally friendly and non-toxic agents such as inert gases; however, their use requires high quantities for effective suppression [8]. On the other hand, novel agents such as metal-based compounds, for example, have demonstrated a high efficiency, in some cases higher than Halon 1301. Nevertheless, their toxicity and a lack of understanding of their mechanisms have limited their application [9]. Despite of all these efforts to find a suitable Halon 1301 substitute, no substance has yet been found to meet all the criteria [8]. This dilemma suggests a necessity for further understanding of fire suppressant mechanisms that help us to identify better alternatives.

As a result, the present work aims to obtain a better understanding of Halon 1301 inhibition mechanisms by studying its effects on methane premixed combustion. For this, determination of important parameters, such as ignition delay times and OH* time histories, were carried out by numerical and experimental analysis. Details of the experimental apparatus and procedure are given below, followed

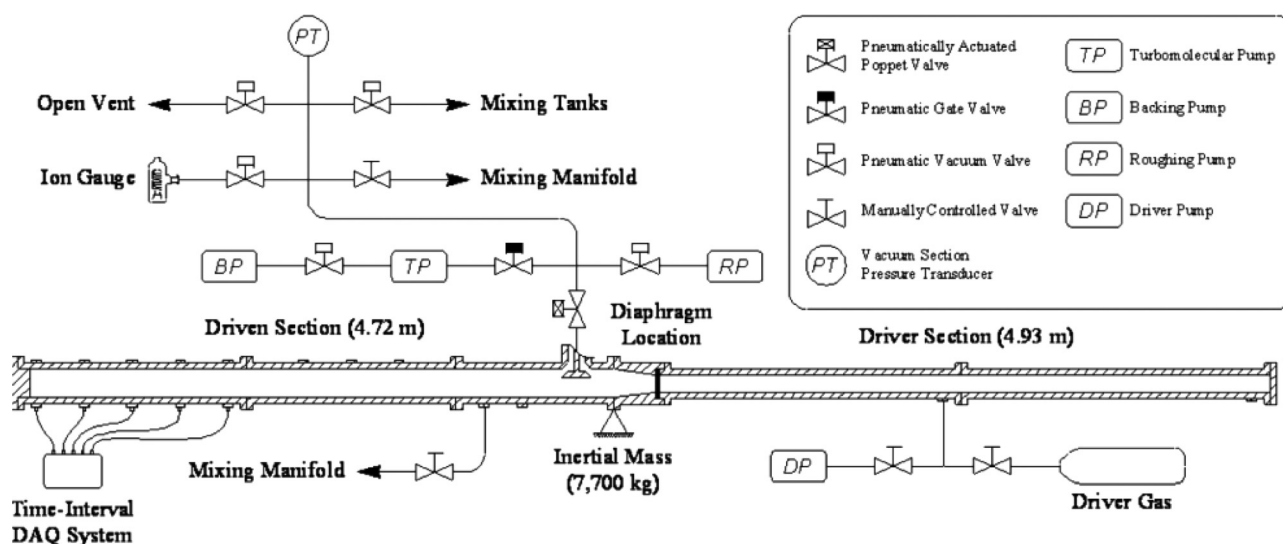


Figure 1. Schematic representation of the High Pressure Shock Tube (HPST) facility at Texas A&M University, taken from Aul et al. [10]

by a description of the chemical kinetics model employed herein. The results of the experiments are presented next, including comparisons with the model.

EXPERIMENTAL

Shock tubes have been widely used for several decades as a valuable tool to gain understanding of chemical kinetics mechanisms. In this work, experimental measurements were carried out using the High Pressure Shock Tube facility (HPST) at Texas A&M University. This facility, described in more detail by Aul et al. [10], presents an integral design that can provide highly repeatable test conditions and controllable experiments. The HPST facility, shown in Figure 1, is provided with driven and driver

sections that have an ID of 15.24 cm and 7.62 cm, respectively, both with a 1.27 cm wall thickness, constructed entirely of stainless steel 304. The two sections are separated by a diaphragm that ruptures depending of the pressure ratio between these two sections. This ratio defines the incident shock wave velocity and therefore the conditions behind reflected shock wave.

Incident shock wave velocity is obtained by using pressure transducers located along the shock tube and a set of timer counters. By this means, it is possible to determine the reflected shock wave conditions which are calculated using the standard 1-D shock relations. Reaction progress is monitored using sidewall emission measurements of OH* chemiluminescence at 310 nm, through a window located 1.6 cm from the end wall. Additionally, this system employs a photomultiplier tube and a narrow-band filter that allows the signal to be amplified, which is then sent to a GageScope computer data acquisition system. In order to determine the ignition delay time (τ_{ign}), pressure/OH* emission time histories were used.

As shown in Figure 2, τ_{ign} is defined as the time when the optical emission shows a rapid increase, signifying the

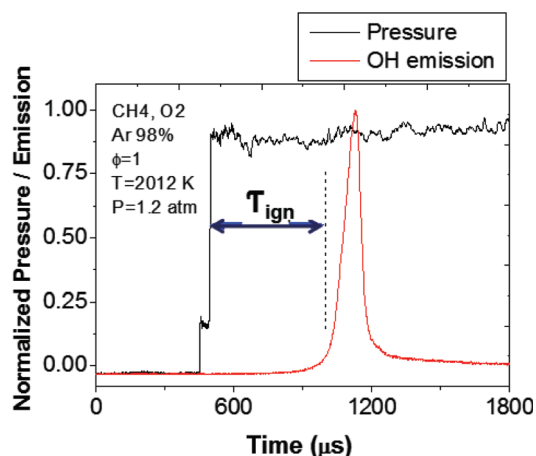


Figure 2. Typical Pressure/OH* emission oscillogram obtained using the HPST at Texas A&M University

Table 1. Experimental mixtures composition (%); balance is Argon. Φ is the fuel-to oxidizer equivalence ratio.

Mixture	Φ	CF ₃ Br/CH ₄ ratio	CH ₄ (%)	CF ₃ Br (%)	O ₂ (%)
1	1	–	0.67	0	1.33
2	1	1/50	0.67	0.01	1.33
3	1	1/20	0.67	0.03	1.33
4	1	1/10	0.67	0.06	1.33

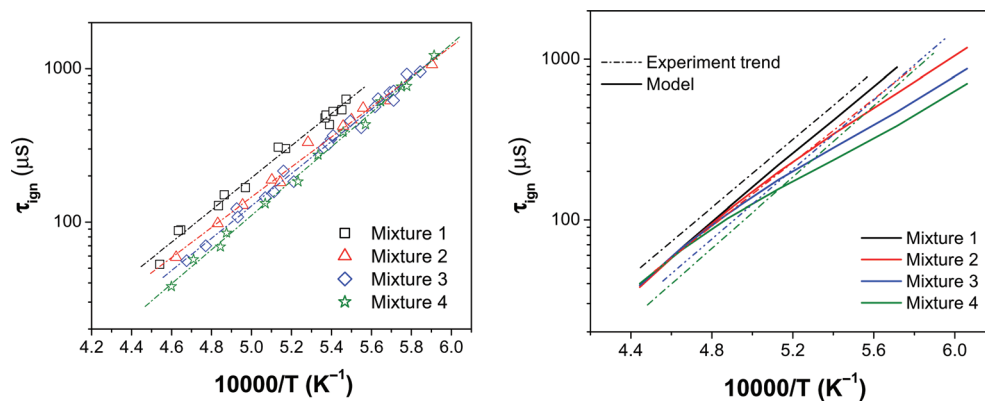


Figure 3. Experimental (left) and modeled (right) ignition delay times (τ_{ign}) on Arrhenius plots

buildup of radicals at the time of reaction; time zero for the experiment is defined as the rise in pressure due to the reflected shock wave. Determination and comparison of other parameters, such as Peak OH^* and Full Width at Half Maximum, required identical optical settings in all tests.

This approach allows reaching premixed, zero-dimensional combustion condition behind reflected shock wave. A wide range of pressures and temperatures can be obtained. However, this study only focuses on atmospheric pressure, since practical fires mostly occur under this

condition. Different stoichiometric mixtures of CH_4/O_2 were prepared using small amounts of CF_3Br , highly diluted in Argon (Table 1).

CHEMICAL KINETICS MODELING

Kinetics modeling for the zero-dimensional problem was performed employing Chemkin[®] [11]. To model the most similar conditions behind a reflected shock wave, the homogeneous batch reactor routine was assumed, with volume

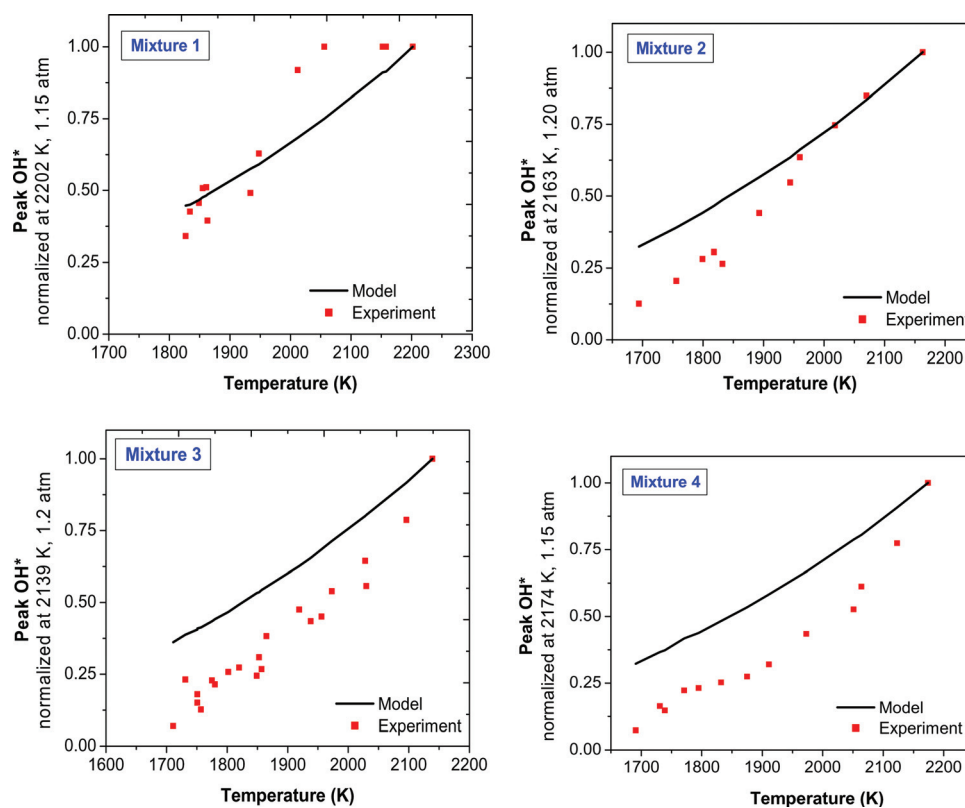


Figure 4. Normalized Peaks OH^* for the different mixtures

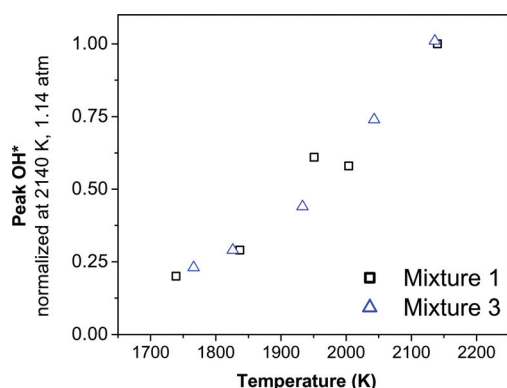


Figure 5. Peak OH* comparison between mixture 1 and Mixture 3

and internal energy as constants. The methane detailed mechanism was modeled using the Gas Research Institute's GRI-Mech 3.0 [12]. To model the time history of the OH*, this model also included the OH* chemistry sub mechanism provided by Hall and Petersen [13]. CF₃Br chemistry was obtained by Westbrook [14].

RESULTS

Experimental and numerical approaches were used to determine the Ignition Delay Times (τ_{ign}) of the different mixtures over a range of temperatures from 1650–2250 K at atmospheric pressure. As shown in Figure 3, experimental and modeled data demonstrated that CF₃Br acts by decreasing the τ_{ign} on methane premixed combustion. However, modeled results show CF₃Br to have a slightly stronger promotion effect (right), compared with experimental data (left).

This study also compares the peak OH* concentrations of each set of experiments with those obtained by modeling at the same conditions. For comparison purposes, each data point was normalized to the test with the hottest temperature. Results show good agreement

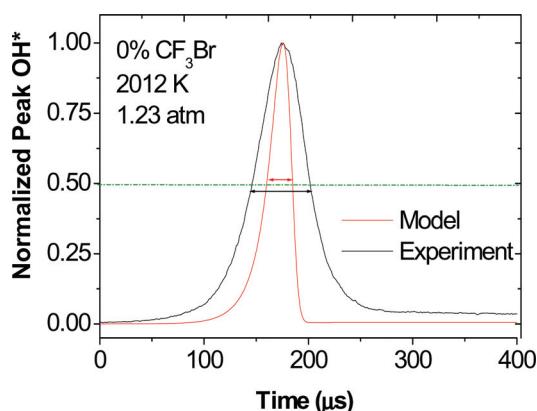


Figure 6. Example of a normalized experimental and modeled peak OH* for the determination of the FWHM

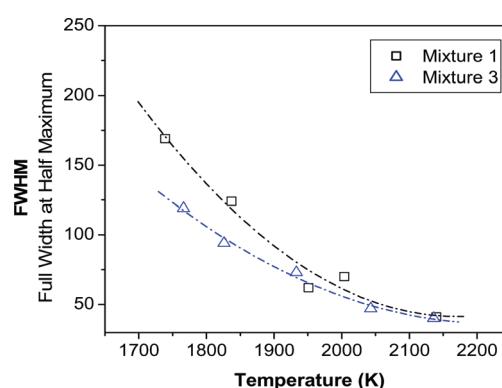


Figure 7. Comparison of the FWHM obtained on experimental tests for mixture 1 and 3

between experimental and modeled data for the methane/oxygen system (mixture 1). However, it can be seen that the model over estimates the values of the experimental peak OH*, for those mixtures containing CF₃Br. Figure 4 shows the normalized peak OH* of the each of the mixtures. Comparison of peak OH* between different mixtures does not show significant changes. Figure 5 compares experimental peak OH* of mixtures 1 and 3. For this direct comparison, it was necessary identical optical settings in all these tests since the observed voltage level is sensitive to the optical solid angle of the detection system.

Additionally, the Full Width at Half Medium (FWHM) of the OH* time histories was analyzed. This parameter provides information on how fast the OH* is produced and consumed. It means, a higher FWHM values, the production or consumption of OH* is slower. For this analysis, each experiment and its model were normalized to 1 as shown in Figure 6. Results show a decreasing of FWHM by the action of Halon 1301, as it can be seen in Figure 7. On the other hand, Figure 8 shows that the model underestimates the data observed from the experiments.

CONCLUSIONS

Due to the difficulty of finding a suitable Halon 1301 replacement, it is necessary to improve our understanding of the CF₃Br inhibition mechanism. For this reason, experimental and modeling approaches were carried out to determine important combustion parameters such as ignition delay time. Additionally, other parameters such as peak OH* and Full Width at Half Medium (FWHM) of the OH* time histories has been proposed as tools for fire inhibition mechanism studies. These parameters were used herein to examine the effect of CF₃Br on methane combustion, as well as metrics for mechanism validation.

Analysis of the ignition delay times on experimental and modeled data show that CF₃Br actually promotes the ignition process by decreasing the ignition time. Similarly, it was observed a decreasing of FWHM by the action of Halon 1301. However, no significant changes on peak OH*

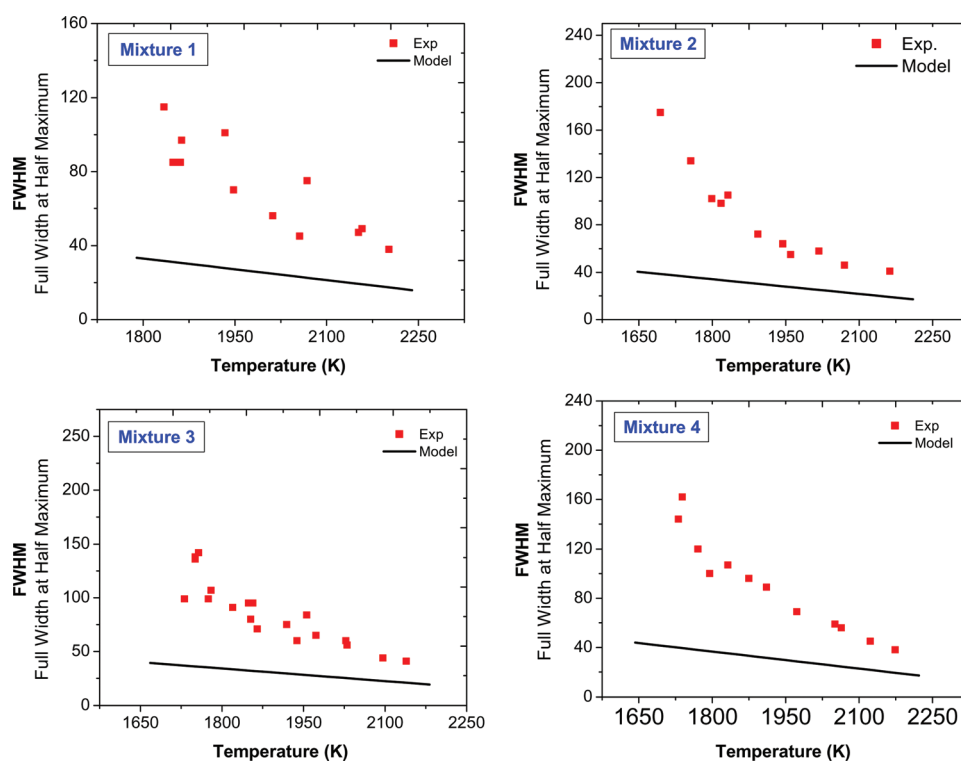


Figure 8. Normalized Peaks OH* as a function of temperature for the different mixtures, compared to predictions of the model

were observed. Comparison between experimental and modeled data shows that the CF₃Br mechanism behaves rather well; however, there are still some numerical disagreements that could be improved. A final predictive model could include predictions for other combustion properties, such as shock-tube ignition delay times, and history species profiles that help to understand the effect of CF₃Br on methane combustion. With the data herein, an improved mechanism for CF₃Br in methane combustion systems can be formulated, and insight gained using the final mechanism will help to characterize the chemical details of Halon 1301 which may lead to the identification of an effective replacement.

REFERENCES

- Harrison, J.S., D. Strong, R. Scott, M. Davey, Morgan, C., *The Use of the Halon 1301 for Firefighting in Confined Spaces*. Occupational Medicine, 1982. **32**(1): pp. 37–43.
- Committee on Assessment of Fire Suppression Substitutes and Alternatives to Halon, N.S.B., Commission on Physical Sciences, Mathematics, and Applications National Research Council., *Fire Suppression Substitutes and Alternatives to Halon for U.S. Navy Applications*. 1997, Washington, D.C: National Academy Press.
- McCulloch, A., *CFC and Halon replacements in the environment*. Journal of Fluorine Chemistry, 1999. **100**(1-2): pp. 163–173.
- Molina, M., Rowland, F., *Stratospheric Sink for Chlorofluoro-methane: Chlorine Atom Catalysed Destruction of Ozone*. Nature, 1974. **249**.
- Daniel, J.S., et al., *Stratospheric ozone destruction: The importance of bromine relative to chlorine*. J. Geophys. Res., 1999. **104**(D19): pp. 23871–23880.
- UNEP, *Montreal Protocol on Substances that Deplete the Ozone Layer. Final Act.*, U.N.E.P. (UNEP). Editor. 1987: Montreal, Canada.
- Clean Air Act in VI*, U.S. Code, Editor. 1990.
- NIST, *Fire Suppression in Aircraft*, ed. R.G. Gann. 2007: National Institute of Standards and Technology (NIST).
- Linteris, G.T., *Flame Suppression Chemistry*, in *Fire Suppression in Aircraft: The Final Report of the Next Generation Fire Suppression Technology Program*, R.G. Gann, Editor. 2007, National Institute of Standards and Technology (NIST).
- Aul, C.J., DeVries, J. and Petersen, E. L. *New Shock Tube Facility for Studies in Chemical Kinetics at Engine Conditions*. in *Eastern States Fall Technical Meeting of the Combustion Institute*. 2007. Charlottesville, VA.
- Kee, R.J.R., F.M., Miller, J.A., Coltrin, M.E., Grcar, J.F., Meeks, E., Moffat, H.K., Lutz, A.E., Dixon-Lewis, G., Smooke, M.D., Warnatz, J., Evans, G.H., Larson, R.S., Mitchell, R.E., Petzold, L.R., Reynolds, W.C., Caracotsios, M., Stewart, W.E., Glarborg, P., Wang, C., and Adigun, O.,

- Chemkin Collection, Release 4.1.1*, I. Reaction Design, Editor. 2007: San Diego, CA.
12. Smith, G.P., Golden, D.M., Frenklach, M., Moriarty, N.W., Eetherneer, B., Goldenberg, M., Bowman, C.T., Hanson, R.K., Song, S., Gardiner, W.C. Jr., Lissianski, V.V., and Quin, Z., *GRI-Mech 3.0*. Available from: <http://www.me.berkeley.edu/gri-mech/>.
 13. Hall, J.M. and Petersen, E. L., *An Optimized Kinetics Model for OH Chemiluminescence at High Temperatures and Atmospheric Pressures*. International Journal of Chemical Kinetics, 2006. **38**(12): pp. 714–724.
 14. Westbrook, C.K., *Numerical Modeling of Flame Inhibition by CF₃Br*. Combustion Science and Technology, 1983. **34**: pp. 201–225.