

Shock-tube study of the addition effect of CF_2BrCl on the ignition of light hydrocarbons

O. Mathieu, C. Gregoire, and E. L. Petersen
Texas A&M University, Department of Mechanical Engineering
College Station, Texas, USA

1 Introduction

After the Montreal protocol in 1987, many efficient fire suppressants have been phased out due to their ozone-depleting properties [1]. Two of the most important agents that have been banned, in terms of both efficiency and usage, were CF_3Br (Halon 1301) and CF_2BrCl (Halon 1211). Although the production of these two components was stopped, it is worth mentioning that their usage is still allowed through recycling and that Halon 1211 is still widely used in many applications, notably in the military and aviation areas.

To limit their usage to the most efficient way and to find suitable replacements, it is therefore necessary to understand the details of their chemical effects during combustion. While CF_3Br has been the topic of numerous studies [2, 3], it is worth mentioning that, to the best of the authors' knowledge, there is no experimental or numerical study of the effects of Halon 1211 on the combustion of any fuel. One can however mention the studies from Yu et al. where the high-temperature chemistry of CF_2BrCl in pyrolysis with [4] and without [5] hydrogen was investigated.

To help in the development of models and to assess the effect of Halon 1211 on light hydrocarbons of interest for many industries, ignition delay times (τ_{ign}) of methane, ethylene, and propane, doped with the equivalent to 10% of the fuel concentration as Halon 1211, have been measured in a shock tube. Mixtures were highly diluted in Ar (around 98% dilution by volume), and a large range of equivalence ratios (ϕ) was investigated (0.5, 1.0, and 2.0) at a pressure around 1.8 atm. Results from the present study were compared to data recently obtained by the authors' group with other fire suppressants, namely CF_3Br (Halon 1301) addition to methane and propane from Osorio et al. [3] and CF_3I (Halon 13001) addition to methane, ethylene, and propane from Mathieu et al. [6]. Note that since Osorio et al. did not study CF_3Br addition to ethylene, this mixture of CF_3Br with C_2H_4 was also investigated during the present study to allow for a direct comparison between the effects of the two agents. Presented in the sections below are details on the experimental setup, followed by a presentation and discussion of the results.

2 Experimental setup

Ignition delay times were measured in a stainless steel shock tube. The driver section is 2.46 m long (76.2 mm i.d.), and the driven section is 4.72 m long (152.4 mm i.d.). The measurement section is equipped with 5 pressure transducers (PCB P113A, equally spaced by 406 mm) mounted flush with

the inner surface of the tube, the last one being 16 mm before the shock-tube end wall. The incident shock wave velocities were determined using signals delivered by these transducers and four Fluke PM-6666 timer/counter boxes. The incident wave speed at the endwall location was then determined using a curve fit of these four velocities extrapolated to the endwall. Post reflected-shock conditions (Temperature (T_5) and Pressure (P_5)) were obtained using this extrapolated wave speed in conjunction with one-dimensional shock relations and the initial conditions at the test region. In the same plane as the last pressure transducer, a sapphire window (9.9 mm optical diameter and 9.8 mm thickness) allows light from the combustion process to fall upon the optical setup, described below. Test pressure was monitored by one PCB 134A transducer located at the endwall and one Kistler 603 B1 transducer located at the sidewall. More details and schematics of the experimental setup are available in Aul et al. [7].

The shock tube and associated tubing are connected with a primary vacuum pump and a Varian 551 Turbomolecular pump, which allow for the whole experimental setup to be vacuumed to 2×10^{-5} Torr or better before every run. The mixtures were prepared in a mixing tank using the partial pressure method. The gases (CH_4 (99.97%), C_2H_4 (99.995%), O_2 (99.999%), C_3H_8 (99.5%), CF_2BrCl (>99%), and Ar (99.999%)) were passed through a perforated stinger traversing the center of the mixing tank to allow for rapid, turbulent mixing. Mixtures and conditions investigated during the course of this study are visible in Table 1.

Table 1: Mixtures and conditions investigated during this study.

Fuel	ϕ	CF_2BrCl (%)	Fuel (%)	O_2 (%)	Ar (%)	P_5 (atm)	T_5 (K)
CH_4	0.5	0.04	0.40	1.60	97.96	1.80	1510-1790
	1.0	0.0667	0.667	1.333	97.9333	1.70	1585-2075
	2.0	0.10	1.00	1.00	97.90	1.70	1695-2010
C_2H_4	0.5	0.0286	0.286	1.714	97.9714	2.00	1260-1450
	1.0	0.05	0.50	1.50	97.95	1.96	1300-1575
	2.0	0.08	0.80	1.20	97.92	1.83	1425-1700
C_3H_8	0.5	0.0182	0.182	1.818	97.9818	1.90	1325-1540
	1.0	0.0333	0.333	1.667	97.9667	1.87	1400-1630
	2.0	0.0571	0.571	1.429	97.9429	1.80	1495-1745
Fuel	ϕ	CF_3Br (%)	Fuel (%)	O_2 (%)	Ar (%)	P_5 (atm)	T_5 (K)
C_2H_4	0.5	0.0286	0.286	1.714	97.9714	1.95	1255-1555
	1.0	0.05	0.50	1.50	97.95	1.87	1315-1620
	2.0	0.08	0.80	1.20	97.92	1.86	1415-1700

3 Results

The ignition delay time was defined as the time between the passage of the reflected shock wave and the intersection of lines drawn along the steepest rate-of-change of OH^* de-excitation (i.e., chemiluminescence) and a horizontal line which defines the zero-concentration level, as visible in Fig. 1. The emission spectroscopy from the $\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi$ transition of the excited-state hydroxyl radical (OH^*) was followed at the sidewall location 16 mm from the endwall using an interference filter centered at 307 ± 10 nm with a Hamamatsu 1P21 photomultiplier tube in a custom-made housing.

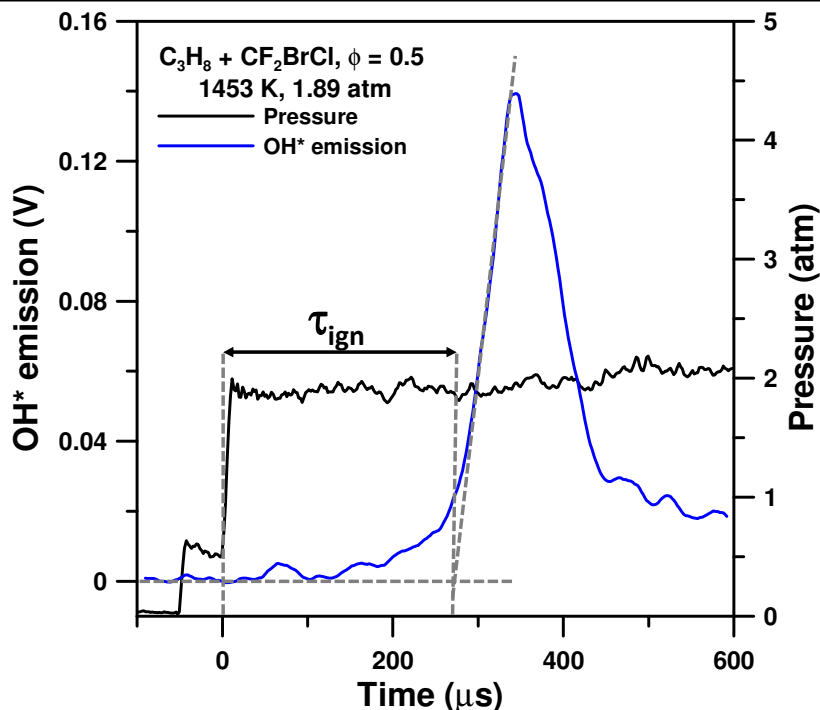


Figure 1. Method of determination of the ignition delay time.

Uncertainties in τ_{ign} are primarily due to the uncertainty in reflected-shock temperature determination, which is below 10 K (see [2-7]). As a result, the uncertainty in τ_{ign} reported in this study is around 10%. This uncertainty level also takes into account the non-ideal boundary layer effects measured by the change in pressure (dP/dt) behind reflected shock waves.

The ignition delay time results for each of the hydrocarbon fuels are presented in the following subsections. Note that chemical kinetics modeling of the results is an important part of the overall study but are not contained in the present extended abstract. Details on the chemical kinetics modeling will be presented in a follow-up paper.

Ignition delay times for methane:

The effect of Halon 1211 on the ignition delay time for methane is visible in Fig. 2 at (a) $\phi = 0.5$, (b) $\phi = 1.0$, and (c) $\phi = 2.0$. As can be seen, adding CF_2BrCl to the mixture induces a strong increase in the reactivity: the ignition delay time is decreased by a factor larger than 6 at the fuel lean condition and by factors around 3 and 2 for the stoichiometric and fuel rich case, respectively. These results were also compared with recent data for CF_3Br [3] and CF_3I [6] addition over similar conditions. As can be seen, under the conditions investigated, Halon 1211 has a larger effect on methane ignition than both Halon 1301 (CF_3Br) and Halon 13001 (CF_3I) since ignition delay times for the two other fire suppressants are between those of neat methane and those for methane seeded with CF_2BrCl .

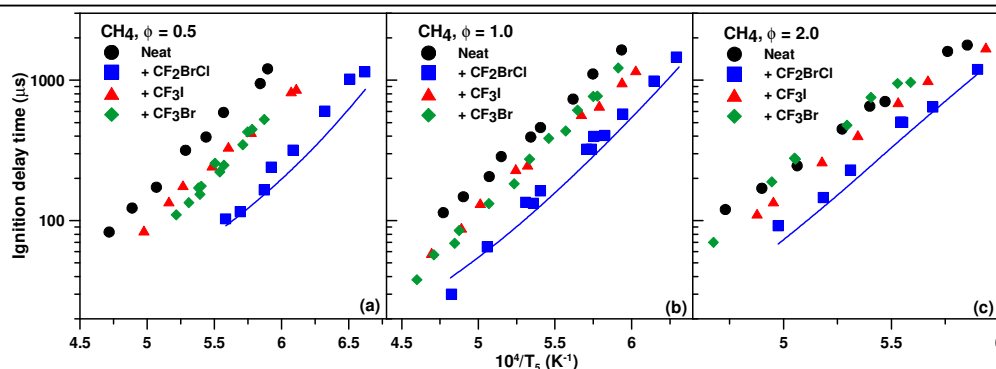


Figure 2. Effect of fire suppressant addition on CH_4 ignition at around 1.8 atm for (a) $\phi = 0.5$, (b) $\phi = 1.0$, and (c) $\phi = 2.0$. Neat CH_4 and CF_3I addition data are from Mathieu et al. [6]; CF_3Br addition data are from Osorio et al. [3]. Lines: model (present study).

Ignition delay times for ethylene:

The effects of CF_2BrCl addition on the ignition of ethylene are visible in Fig. 3 (a)-(c), for ϕ ranging from 0.5 to 2.0, respectively. As can be seen, the addition of Halon 1211 tends to increase the ignition delay time, mostly on the low-temperature side, and this effect grows with the increase in the equivalence ratio: at the coldest temperature investigated for each condition, the ignition delay time is increased by factors around 2.4, 2.7, and 4 at $\phi = 0.5$, 1.0, and 2.0, respectively. It is however interesting to note that although the CF_2BrCl addition increases the ignition delay time over the entire range of temperature investigated for the fuel rich (c) condition, the ignition delay times are similar between the neat and fire suppressant addition around 1135 K for the stoichiometric (b) case; and the ignition delay times are even shortened by the presence of CF_2BrCl above 1380 K at $\phi = 0.5$ (a). Results with CF_3I and CF_3Br are very similar to those for Halon 1211; one can however notice that the increase in the ignition delay time seems higher with CF_3I at low temperature, and that the ignition delay time does not seem to be reduced by CF_3I and CF_3Br on the high-temperature side of the fuel lean case.

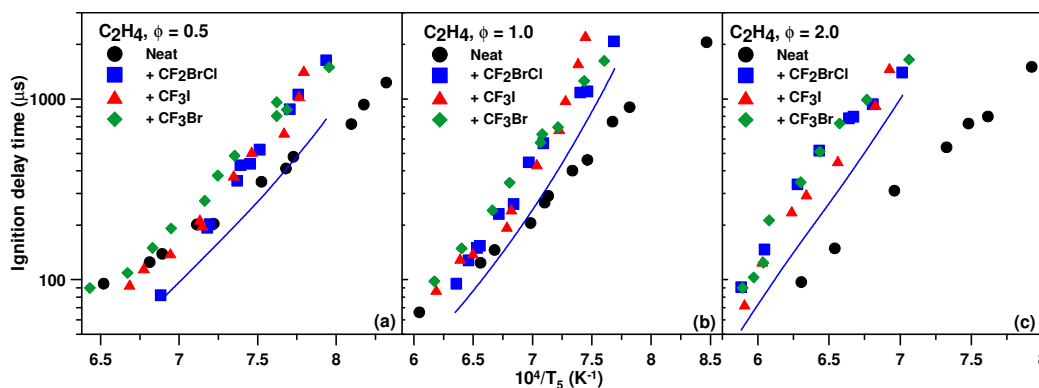


Figure 3. Effect of fire suppressant addition on C_2H_4 ignition at around 1.8 atm for (a) $\phi = 0.5$, (b) $\phi = 1.0$, and (c) $\phi = 2.0$. Neat C_2H_4 and CF_3I addition data from Mathieu et al. [6]. Lines: model (this study).

Ignition delay times for propane:

Figure 4 presents the effects of CF_2BrCl on C_3H_8 ignition at (a) $\phi = 0.5$, (b) $\phi = 1.0$, and (c) $\phi = 2.0$. As can be seen, Halon 1211 addition has little influence on the ignition delay time of propane: results are nearly unchanged at $\phi = 0.5$ (at 20% increase in observed on the low-temperature side only), and a

small increase in the ignition delay time is observed at $\phi = 1.0$ (between 20% at high temperature and 45% at low temperature). For the fuel rich case, a noticeable increase in the ignition delay time is observed over the entire range of temperature investigated (between a factor 1.6 at high temperature and 2.0 at low temperature). By comparison, CF_3Br has a larger effect in increasing the ignition delay time over the range of conditions investigated. CF_3I results are similar to those of CF_2BrCl , except for the fuel rich case where CF_3I slightly reduces the reactivity of the mixture at the end of the low-temperature side only.

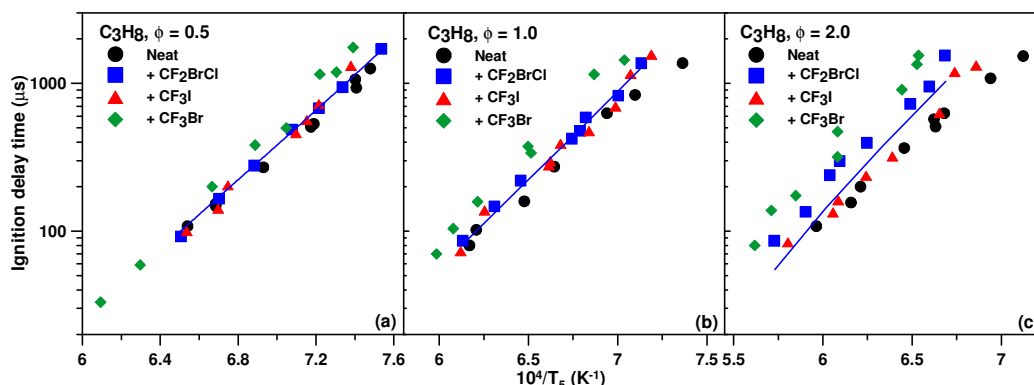


Figure 4. Effect of fire suppressant addition on C_3H_8 ignition at around 1.8 atm for (a) $\phi = 0.5$, (b) $\phi = 1.0$, and (c) $\phi = 2.0$. Neat C_3H_8 and CF_3I addition data are from Mathieu et al. [6], and the CF_3Br -addition data are from Osorio et al. [3]. Lines: model (this study).

4 Modeling

A CF_2BrCl model was assembled from literature's mechanisms [4-5, 8-9] while the missing reactions have been added from both the literature and from estimates (by similarities) for reactions that have never been measured nor calculated before. Results for CH_4 , C_2H_4 , and C_3H_8 are visible in Figs. 2, 3, and 4, respectively. As can be seen, data with methane are satisfactorily predicted, within 30% accuracy, although the model is slightly over-reactive. Data with C_2H_4 are typically under-predicted by a factor around 2 or lower and the data with C_3H_8 are very well predicted for lean and stoichiometric conditions. The model is also slightly over-reactive for fuel rich condition (up to 40% difference in the ignition delay time). Sensitivity and reaction pathway analyses were conducted with the model to explain the results from this study. These analyses showed that with propane and ethylene, the inhibiting effect of Halon 1211 on the ignition delay time is essentially due to the consumption of H radicals through the reaction $\text{HBr} + \text{H} \rightleftharpoons \text{Br} + \text{H}_2$, which then inhibits the branching reaction $\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$. In the case of methane, the radical CF_2 promotes the formation of radical H by reacting with CH_3 ($\text{CH}_3 + \text{CF}_2 \rightleftharpoons \text{CH}_2\text{CF}_2 + \text{H}$). This radical H then reacts with O_2 , and promotes the reactivity through the branching reaction $\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$.

4 Conclusion

Ignition delay times of small hydrocarbons with Halon 1211 have been measured for the first time in a shock tube. Effects of CF_2BrCl on τ_{ign} are strongly fuel dependent: an important decrease in the ignition delay time was observed with CH_4 , whereas an increase in τ_{ign} was observed for the two other fuels. The importance of this increase is however dependent on the temperature (larger increase on the low-temperature side in most cases) and the equivalence ratio (the higher the equivalence ratio, the

bigger the fire suppressant effect). Compared to other fire suppressants, namely CF_3Br and CF_3I , Halon 1211 showed a larger effect with methane; similar results with ethylene; and an effect that is more important than CF_3I but smaller than CF_3Br with C_3H_8 . A tentative model was assembled and presents satisfactory predictions overall. The experimental trends have been explained using this model. The present results illustrate the necessity for understanding the details behind the chemical effects of these agents on the combustion of hydrocarbons to select the most suitable agent or blend of agents depending on the application.

5 Acknowledgments

During this study, Claire Grégoire was a visiting researcher at Texas A&M University from Université d'Orléans, France.

6 References

-
- [1] Montreal Protocol on Substances that Deplete the Ozone Layer, Final Act, United Nations Environmental Program (UNEP), Montreal, Canada, 1987.
 - [2] Noto T et al. (1998). Inhibition effectiveness of halogenated compounds. *Combust. Flame* 112: 147.
 - [3] Osorio CH et al. (2013). Effect of CF_3Br on C1–C3 ignition and laminar flame speed: Numerical and experimental evaluation. *Combust. Flame* 160: 1044.
 - [4] Yu H et al. (2005). Experimental and Computational studies of the gas-phase reaction of Halon 1211 with Hydrogen. *Environ. Sci. Technol.* 39: 3020.
 - [5] Yu H et al. (2005). Experimental and Computational studies of the thermal decomposition of Halon 1211. *Int. J. Chem. Kinet.* 37: 134.
 - [6] Mathieu O et al. (2014). Experimental study of the effect of CF_3I addition on the ignition delay time and laminar flame speed of methane, ethylene, and propane. *Proceed. Combust. Inst.*, In Press
 - [7] Aul CJ et al. (2013). Ignition and kinetic modeling of methane and ethane fuel blends with oxygen: A design of experiments approach. *Combust. Flame* 160: 1153.
 - [8] Metcalfe, WK et al. (2013). A Hierarchical and comparative kinetic modeling study of C1 – C2 hydrocarbon and oxygenated fuels. *Int. J. Chem. Kinet.* 45: 638.
 - [9] Babushok, VI et al. (2014). Flame inhibition by CF_3CHCl_2 (HCFC-123). *Combust. Sci. Technol.* 186: 792.