FLAME RETARDANTS EFFECTIVENESS IN GASEOUS DETONATION MITIGATION

P.J. Van Tiggelen and M.H. Lefebvre
Laboratoire de Physico-Chimie de la Combustion, Université Catholique de Louvain
1348 Louvain-La-Neuve, Belgium

ABSTRACT

For combustion phenomena the role of inhibition in reducing the burning velocity of flammable mixture is of paramount importance and has been well documented. But, when the combustion process is supported by detonation waves in gases, the precise role of chemical and physical factors is not clearly defined. In this paper the following question is addressed: does it exist specific chemical actions of some compounds either to mitigate or to suppress completely gaseous detonation waves? After reviewing the self-sustainance mechanism of gaseous detonations, the influence of flame retardants will be discussed taking into account thermal as well as chemical factors of several halogenated compounds. The interaction between the fuel and the inhibitor will he also examined. Data about structure and velocity of detonation waves will be presented, and the importance of the overall heat capacity of the fresh gases mixture will be discussed. The study focuses on potential substitutes of CF_3Br. Thirteen different halogenated species have been investigated and rated according to their efficiency to mitigate detonation waves.

1.0 INTRODUCTION

Halons have been used traditionally in many fire suppressing applications with great success. But, since the Montreal Protocol those compounds have been phased out without real substitutes with similar efficiency. Many papers have been devoted to the applications of halon substitutes in flame and fire extinguishments, among them are Richter et al. [1] and Noto et al. [2]. However, in the explosion regime of detonations, there are very few studies concerning that problem. It is indeed, much more difficult to impede the transition from flame process toward violent explosions. In this paper we address the question of the inhibitor influence on well-developed detonation. The structure of gaseous detonations has been largely investigated in the past [3,4]. The key feature of the structure of the front is the transverse wave, a shock joined to the leading shock through the classical three-shock configuration: the Mach stem and the incident shock are part of the leading shock and the transverse wave is the reflected shock. They are nonsteady waves and are continually decaying; they stay alive only by periodic reignition of the reactive mixture through collision with other transverse waves moving in the opposite direction. Hence, the cellular structure is self-sustaining, with the chemical reaction being the driving force. The characteristics of the detonation wave (cell size) can be correlated to physico-chemical characteristics of the exploding mixtures (induction times, lengths of the heat release zone). The length of the detonation cell depends much on the initial conditions of the detonating mixture and on the oxidation process, see for instance Lihouton et al. [5]. The aim of this paper is to investigate the influence of the occurrence of halogenated species on the exploding behavior of reference reacting mixtures. Halons have been used largely in commercial and military applications as fire extinguishing agent, although they have high ozone depleting potentials. Their manufacture has been banned by the Montreal Protocol on Substances That Deplete the

Ozone Layer, and many investigations are currently carried out to develop ozone-friendly chemicals that could be used as halon replacements. The inhibition efficiency of halogenated compounds in flames has been analyzed recently by Noto et al. [2]. The influence of several halocompounds on the burning velocity of C_1-C_2 hydrocarbon flames was investigated. An exponential inhibition parameter was used to classify the merit of different additives. An important chemical action of CF_3Br and CF_3I on flame propagation was demonstrated, as well as a decrease of their relative chemical influence when the additive concentration is increased. Noto et al. [2] recommend also the use of a "composite" inhibitor combining an effective chemical inhibitor with an inert additive characterized by a high heat capacity. Along the same line one should ask the following question: does a specific chemical action of additives exist that mitigates or suppresses the propagation of detonation wave? It is worth mentioning along that line that Lefebvre et al. [6,7] report that typical flame inhibitors have a significant influence on the characteristics of the detonation. The present work presents evidences **of** the inhibiting effect of halogenated compounds on the propagation of the detonation wave. The experimental data will be discussed and illustrated by some numerical calculations.

2.0 DETONATION MODELS

2.1 Physical Models

The basic model for calculating the velocity of a detonation wave is the Chapman-Jouguet (CJ) theory. It is based solely on the three conservation equations in the direction of the propagation, the equation of state, and the CJ criterion that assumes sonic downstream-flow velocity relative to the wave. The **CJ** theory also requires that the equilibrium conditions prevail downstream of the reaction zone. The CJ theory is based on energetics and the chemical rate processes *are* not considered. Hence, the CJ theory can only predict the detonation wave velocity and does not provide any information on the dynamic detonation parameters (detonation limits, cell sizes, induction times, etc.).

The one-dimensional structure of the detonation wave proposed by Zeldovich, von Neumann and Döring (ZND-model) consists of a normal shock followed by an induction zone and a reaction zone. The end of the reaction zone is the CJ or sonic plane with equilibrium states. The ZND model gives a mechanism for the propagation of the detonation, i.e., autoignition by adiabatic shock compression. Knowledge of the reaction mechanism (see next item) and the rate constants permits the detailed time evolution of the thermodynamic states behind the shock to be calculated. The ZND model allows a length **or** time scale (induction or reaction zone thickness) to be determined from chemical kinetics and related to the experimental parameters of the detonation wave. Detailed description of the ZND-model and of calculations of detonation parameters throughout a ZND-detonation wave is given for instance by Ficket and Davis [4].

Alternatives to these relatively simple approaches are numerical simulations including a complete integration of the conservation equations. Many authors are performing this type of computations [8,9,10]. Such computations are time-consuming on the computer and must be coupled to a specific model for the chemical reaction and a simplified kinetics.

2.2 Kinetic Models

The major requirements for integrating a kinetic mechanism to calculate the heat release are the knowledge of the elementary reactions and their rate constants. These calculations are thus currently limited to simulations of detonations in chemically simple mixtures (for example oxygen/hydrogen). Hence this approach is not appropriate for the study of complex reactive systems like mixtures containing halogenated species.

However, the inhibiting effect of the additives can be understood by using a simplified kinetic mechanism and a simple linear model for the calculation of the radical-production rate [11]. Such a simplified kinetic mechanism is shown in Table 1. The primary conversion of the additive occurs through an elementary reaction with H (reaction Sa), OH (reaction 5b), and/or O (reaction 5c). The species 'X' in Table 1 designates any stable product of the primary attack of the additive. The consumption of the additive (Inh.) by radicals H and OH produces an intermediate species much less reactive than the usual chain-carrier radicals (H, OH, O). In the model, HO_2 is assumed to be a nonreactive radical (reaction **6).** When the inhibitor contains a hydrogen atom, the primary attack by 0-atoms may produce an active radical OH (reaction 5c) and reactivate the chain reaction.

Table 1. Simplified kinetic mechanism for H_2-CO-O_2-Ar-Inhibitor mixtures.
X represents products, reactants or slowly reacting radicals.

(0)		$H_2 + O_2$	→	2 OH
(1)		$H + O_2$	→	OH + O
(2)		$O + H_2$	→	OH + H
(3)		$H_2 + OH$	→	$H_2O + H$
(4)		CO + OH	→	$CO_2 + H$
	(a)	H	→	X
(5)	(b)	Inh. + OH	→	X
	(c)	O	→	X + OH
(6)		$H + O_2 + M$	→	$HO_2 + M$

Using a set of linear differential equations for the reaction rate of the chain carrier radicals, one can calculate the overall rate of production for the radicals. Taking into account reactions (Sa), (5b), and (Sc) altogether leads to the following explosion condition:

$$2v_1 - (v_6 + v_{5a})(1+\frac{v_{5c}}{v_2})(1+\frac{v_{5b}}{v_3+v_4}) + \frac{v_1 v_{5c}}{v_2}(1-\frac{v_{5b}}{v_3+v_4}) > 0 \qquad (1)$$

where v_i is the reaction frequency of the ith elementary chemical reaction (Table 1) and is given by the rate constant of the reaction times the concentrations of the stable species, for instance:

$$v_1 = A_1 \cdot e^{-E/RT} \cdot C_{O_2}$$

More details on this kinetic approach have been reported by Evariste et al. [12]. Equation (1) is a typical explosivity condition showing the competition between the branching reaction (1) and the termination reactions (5a-c) and (6) for the chain carrier radicals. One notices in equation (1) a positive contribution of reaction (Sc), which could account for a promoting effect or at least for a reduction of the inhibiting effect of the inhibitor on the combustion process.

3.0 EXPERIMENTAL SETUP

Experiments are carried out in a detonation tube, 11 m long, with a rectangular cross section of 9.2x3.2 cm^2 (Figure 1). The driver and the test sections are separated with a mylar diaphragm. The driver section, 2 m long, is filled up with a stoichiometric hydrogen/oxygen mixture at an initial pressure of 40,000 Pa and is ignited with a hot wire producing a flame that transits to detonation. The test section, 9 m long, contains the investigated mixture at the nominal pressure. A metallic flange with 2.5 cm boring between both sections impedes the development of overdriven detonations in the test section. After a 4-m travel distance in the test section, the detonation is stabilized to its characteristic regime. The detonation velocity is measured by 8 ionization gauges and the shock structure is recorded on soot plates. The mixing of the mixture is achieved during the filling of the tube, and the composition of the gas is controlled using choked conditions through nozzles for each individual gas. A detailed description of the apparatus is given by Libouton et al. [5].

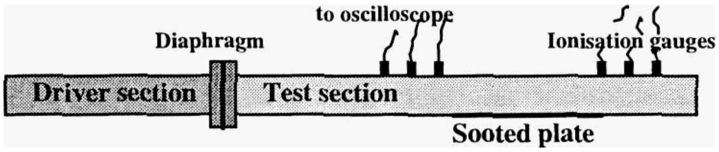

Figure 1. Experimental set up for detonation measurements.

4.0 RESULTS FROM REFERENCE MIXTURES

The most important consideration in choosing a benchmark gaseous detonation system to study is that it has to be one that provides a regular pattern of cells of convenient size. Other considerations are that the kinetics be well understood, so that the observed structures can be correlated with calculated induction times. The mixtures commonly used are hydrogen/oxygen and carbon monoxide/oxygen diluted with inert gases. We chose stoichiometric $H_2/CO/O_2$ diluted with 50 or 30% of Ar. The initial composition is fully defined by the equivalent ratio, Φ, the amount of hydrogen in fuel, β, and the amount of diluent, α. These parameters are expressed in terms of mol fraction X, of species i:

$$\Phi = (X_{H2} + X_{CO})/2X_{O2} \qquad \beta = X_{H2}/(X_{H2}+X_{CO}) \qquad \alpha = X_{Ar}$$

Table 2 gives the initial conditions of the experiments performed with benchmark mixtures and summarizes the experimental results: detonation velocity, D_{exp}, cell length, L, and mode number (the mode number is defined as the number of transverse waves, which is twice the number of cells across the tube section). The Chapman-Jouguet detonation velocity is also mentioned. Figure 2 shows an example of regular cellular pattern for one of the reference compositions (#5).

5.0 EXPERIMENTS WITH MIXTURES CONTAINING HALOGENATED COMPOUNDS

The effect on the detonation propagation of selected halocarbon additives has been investigated experimentally and chemical kinetic calculations have been performed (see next

Table **2.** Initial conditions and experimental results of experiments with the reference mixtures (no halogenated additives in the mixtures).

Series No.	Φ	β	a	P torr	D_{exp} m/s	L cm	mode	D_{CJ} m/s
#1	1.0	1.0	0.50	200	1830	1.1	30	1879
#2	1.0	1.0	0.50	50	1675	7.1	5	1824
#3	1.0	0.25	0.50	75	1488	9.2	4	1622
#4	1.0	0.10	0.50	100	1471	10.5	3	1601
#5	1.0	0.05	0.30	100	1585	7.8	5	1659

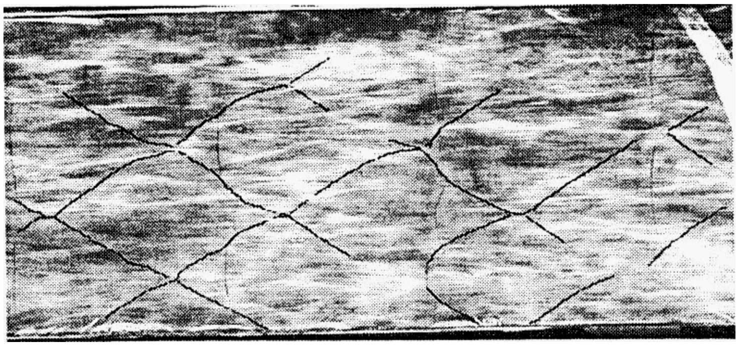

Figure **2.** Soot record printed by the detonation wave of an $H_2/O_2/Ar$-2/1/1.3 mixture at initial pressure 100 torr **(#5)**. The path of the triple shock has been computa-tionally enhanced **to** better visualize the structure. Note the regularity of the cellular structure. The mode number is equal to **5.** The detonation is propagating to the left.

item), namely with bromotrifluoromethane, CF_3Br, chlorodifluoromethane, CF_2HCl, trifluoromethane, CF_3H, and tetrafluoromethane, CF_4. For these additives, kinetic calculations were possible because of the knowledge of or reasonable assumption about the kinetic mechanism. For several other halogenated additives, no reliable kinetic data are available, and we will limit the discussion to the interpretation of the experimental results. The additives tested are the following:

- fluoro- and hydrofluoroalkanes: C_2F_4H, C_2F_5H, and C_3F_8, in addition to the CF_4 and CF_3H
- chloro- and hydrochloro-fluoroalkanes: $CFCl_3$, CF_2Cl_2, CF_3Cl, and C_2F_4HCl, in addition to CF_2HCl
- bromo- and iodoalkanes: CF_2HBr and CF_3I, in addition to CF_3Br

When an additive is added to the corresponding reference mixture to mitigate or to extinguish the detonation, its amount is mentioned with respect to the total mixture and is replacing the same amount of argon. In this case, the dilution factor a is redefined as

$$\alpha = X_{Ar} + X_{inhibitor}.$$

Hence, the additive is considered as **a** diluent for the definition of the stoichiometry although additional hydro-halocarbons modify the actual equivalence ratio Φ slightly.

5.1 Mixtures Containing CF_4 or CF_3H

Those experiments were carried out at initial conditions similar to reference mixture #1, i.e., no CO in the fuel and an initial pressure equal to 200 torr. **Figures** 3(a) and (b) show the detonation velocities **as** function of the additional CF_4 and CF_3H, respectively. The calculated Chapman-Jouguet velocity is **also** plotted on the **figures.** Quite unexpectedly, the experimental velocity D_{exp} exhibits **a** slight increase when we add a few percent **of** CF_4. The effect is not predicted by the CJ-calculation (D_{CJ}). For mixtures containing CF_3H (Fig. 3b), the general trend seems to be in better agreement with the CJ-model. But the limits of detonability **(28%** of CF_3H) are reached well before D_{CJ} starts to decrease **(33%** of additive). Close to the detonability limit, the cell size increases drastically and from **5% of** additive and up, we observe that the regularity of the cell structure deteriorates rapidly, see also Nzeyimana and Van Tiggelen [13].

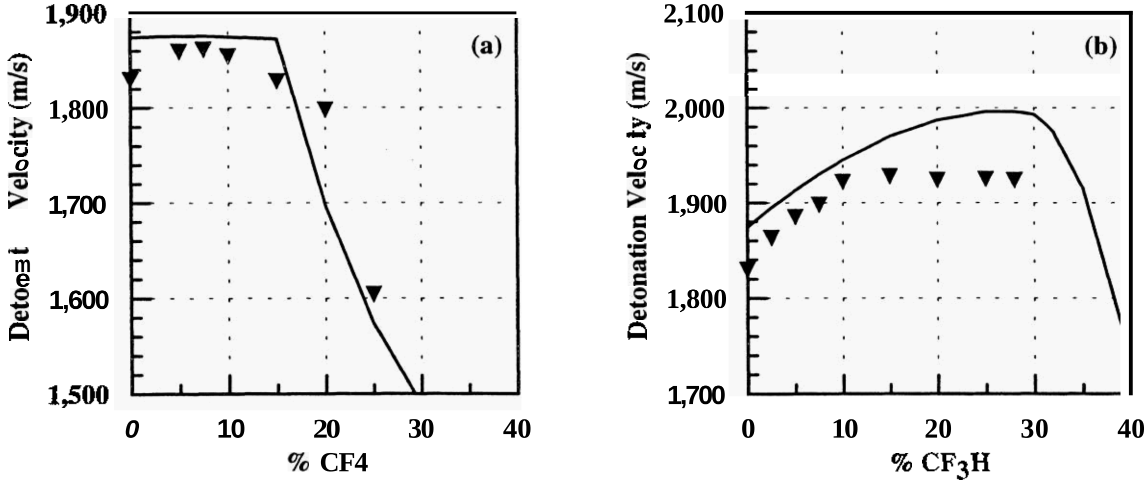

Figure **3.** Experimental (▼) and CJ (solid line) detonation velocities as function of the percentage of added **(a)** CF_4 and (b) CF_3H. The mixture is stoichiometric H_2/O_2 diluted with 50% of (Ar+Inhibitor) at initial pressure equal to 200 torr (reference mixture #1).

5.2 Mixtures Containing CF_3Br, CF_2HBr, CF_2HCl or CF_3H

Experiments presented here are conducted at initial conditions similar to reference mixtures #2, **3,** and 4. Figure 4 summarizes all the recorded detonation velocities and cell lengths for the inhibited mixtures. The influence of the nature of the inhibitor comes out nicely. Larger quantities of additives are necessary to stop the detonation wave when β is large. Furthermore, molecules with bromine atom exhibit a more pronounced inhibiting effect than the one noticed for other fluorocarbon species. This is observed for both detonation velocities and cellular structures. The difference in overall behavior between the CF_3H and CF_2HCl remains minor, though larger amounts of CF_3H are required to affect the detonation wave. Similarly to CF_3Br, the inhibition of CF_2HBr comes from the bromine atom; however, the additional hydrogen atom limits **a** little the inhibition efficiency of CF_2HBr. The experiments

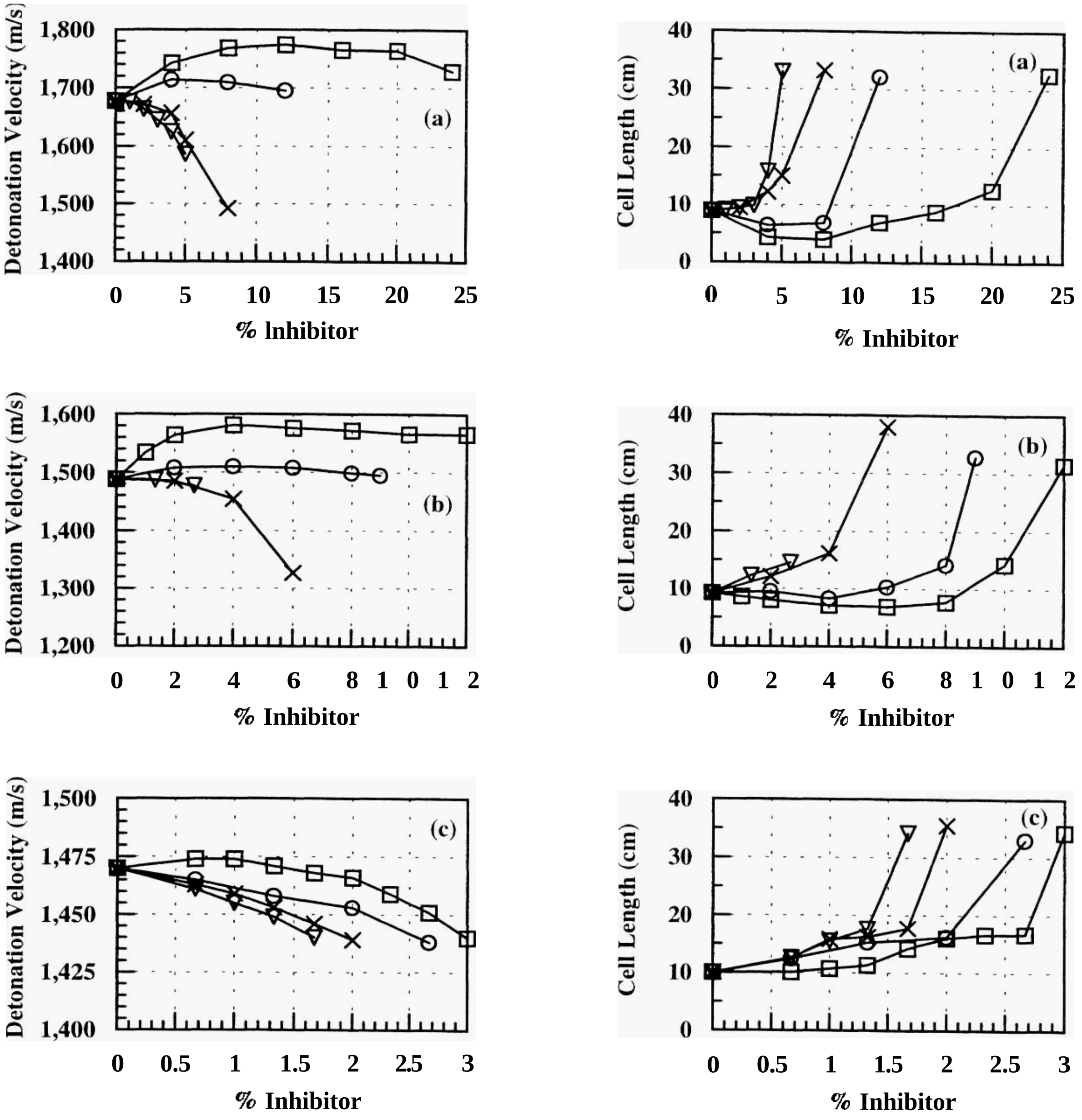

Figure 4. Experimental detonation velocity and detonation cell length as function of the percentage of additive. (a) $\beta = 1.0$ and initial pressure **P** = 50 torr (reference mixture #2), (b) $\beta = 0.25$ and initial pressure **P** = 75 torr (#3), and (c) $\beta = 0.10$ and initial pressure P = 100 torr (#4). The symbols refer to the nature of the inhibitor: ▽ CF_3Br, X CF_2HBr, O CF_2HCl, □ CF_3H.

show that the bromine atom is necessary to decouple the chemical reaction from the leading shock and thus to mitigate and eventually extinguish the supersonic combustion process. For more details, see Evariste and Van Tiggelen [14].

5.3 Comparison of All the Studied Halocarbons

A comprehensive set of halogenated compounds has been tested at initial conditions similar to reference mixture #5 [15]. The values of the detonation velocity and the cell length in the uninhibited reference mixture are 1585 m/s and **7.8** cm (Figure 2), respectively. The evolution of the detonation velocity as a function of the percentage of the halocarbon added in traces is quite sensitive to the amount and the nature of the additive as shown in Figure 5. The evolution of the cell length is consistent with that of the wave velocity. Halogenated compounds have been added up to the extinction of the detonation wave. The largest amount of additive required to extinguish the detonation is **4%** (CF_3H). Because of the small amount of additive, the cellular structure remains quite regular in all those runs, irrespective to the amount of additive in the reference mixture.

Although all additives are slowing down the detonation, they can be classified in thee groups according to their increasing order of efficiency to mitigate the detonation wave:

- **fluoro-** and hydrofluoroalkanes: CF_3H, CF_4, C_2F_4H, C_2F_5H, and C_3F_8
- chloro- and hydrochloro-fluoroalkanes: C_2F_4HCl, CF_2HCl, $CFCl_3$, CF_2Cl_2, and CF_3Cl
- bromo- and iodoalkanes: CF_2HBr, CF_3Br and CF_3I

For hydro-fluorocarbons (HFC) and hydro-chloro-fluorocompounds (HCFC), extinction of the detonation occurs when the content of halogen element (F+Cl) is comparable to the amount of hydrogen element in the mixture. In that case, the fluorine and chlorine atoms are able to scavenge almost all the hydrogen available impeding the detonation to propagate. The lower efficiency of the fluorocarbons (FC) is explainable by the same argument if one keeps in mind that the initial reaction of those compounds by the usual chain carrier radicals (H, **O,** OH) is much slower than the one of the HFCs and HCFCs. The bromo compounds are acting though a chain process recombining the radicals and are thus more efficient than HFCs and HCFCs. Typical reactions are

$$CF_3Br + H \rightarrow CF_3 + HBr \qquad \text{followed by} \qquad HBr + H \rightarrow H_2 + Br$$

6.0 CALCULATIONS

Chapman-Jouguet and ZND-calculations have been performed on reference mixture #1 with CF_4 and CF_3H. Because of the lack of reliable and complete kinetic data for the other type of halogenated compounds, the action of CF_3Br, CF_2HCl, and CF_3H has been studied separately using the simplified linear kinetic model.

6.1 Mixtures Containing CF_4 or CF_3H

Results from the **CJ** calculation and from the kinetic model, for mixtures containing 10% of inhibitors, **are** given in Table **3.** The results shown represent the flow characteristics behind the detonation front at sonic condition. The kinetic mechanism used to integrate the physical parameters throughout the detonation wave according to the ZND-model are described by

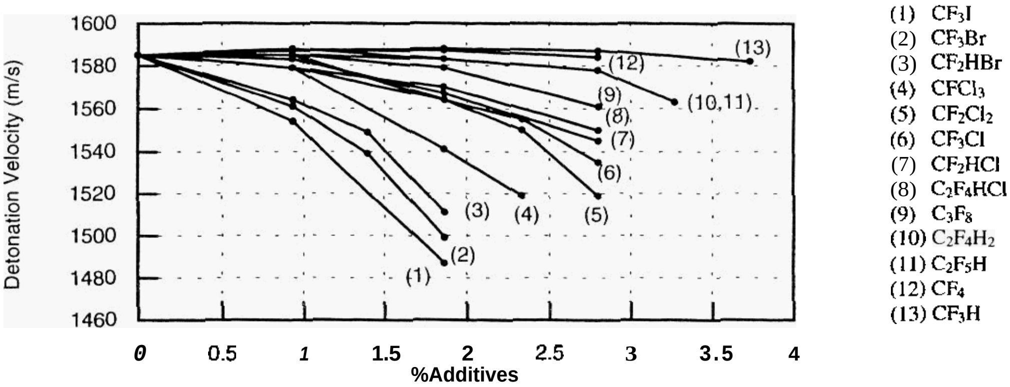

Figure 5. Experimental detonation velocity for mixture #5 containing increasing amount of additives. For each case studied, detonability limits has been achieved.

Lefebvre et al. [6]. **A** detailed report on the detonation product composition and the physical properties of the detonation is given Lefebvre [16]. The calculations (Table **3)** show that it is possible to reach the sonic condition by two different approaches: (1) the classical CJ calculation, which assumes equilibrium composition at the sonic plane, and (2) a time-dependent ZND model, which assumes a kinetic mechanism for the evolution of the species. For the reference mixture (#1- $H_2/O_2/Ar$ in Table 3), the agreement between both calculations is very good. The CJ-assumption of chemical equilibrium is fully appropriate. Significant discrepancies appear when the mixture contains CF_4 or CF_3H. The composition is quite different; the heat released at the sonic plane is much higher when calculated according to a kinetic mechanism than the one calculated with the assumption of chemical equilibrium. From these numerical data, it is obvious that the assumption of chemical equilibrium is not guaranteed for mixtures including fluorocompounds.

6.2 Mixtures Containing CF_3Br, CF_2HCl or CF_3H

In this section, we will discuss the results from calculations using the simplified linear kinetic model described above. Similarly to the experiments conducted with these species, the reference mixtures one has to compare the results to are #2, 3, and 4.

The rate coefficients used for the H_2-CO-O_2 mechanism (reactions **1-4** and 6 in Table 1) are taken from Libouton et al. [11]. The rate coefficients for the inhibiting reactions (5a-c) are given in Table 4 as function of the nature of three of the experimentally studied additives (CF_3Br, CF_2HCl, and CF_3H). Note that no reliable rate coefficients for the inhibition by CF_2HBr were available; consequently, none of the following kinetic calculation involves this species. To investigate the influence of the primary consumption of the inhibitor, we calculate induction times using the data in Table 4. The induction time is defined as the time required to observe the exponential growth of the radical concentrations and is fully suitable for relative comparison between the various mixtures studied. Details about the numerical model are given by Libouton et al. [11]. Figure ***6*** shows the result from the computation for three values of the fuel composition β and represents the induction time as a function of the amount of inhibitor added. The inhibition action of CF_3Br appears clearly in the plots, and CF_3H does not affect the kinetic of the combustion process. The addition of CF_3Br and CF_2HCl results in a sudden increase of the induction time. Drastic increase of the induction time ends up eventually with failure of the

Table 3. Molar fraction and heat release at the sonic condition behind the detonation wave. The reference mixture is mixture #1 (Table 2). Calculations have been carried out according to the Chapman-Jouguet model (CJ) or by integrating a kinetic mechanism through a ZND-detonation wave (Kin).

Mixture:	$H_2/O_2/Ar$		$H_2/O_2/Ar/CF_4$		$H_2/O_2/Ar/CF_3H$	
% Halogen	0		10		10	
Species	CJ	Kin	CJ	Kin	CJ	Kin
H_2	6.7	6.4	1.6	1.4	5.2	7.1
O_2	2.2	2.0	2.4	1.3	0.8	0.2
Ar	55.3	55.0	37.0	40.5	37.0	40.8
CF_4		-	e-13	3.5	-	-
CF_3H	-	-	-		e-12	0.3
H	3.3	4.0	1.2	0.5	2.6	1.0
F	-	-	0.2	-	0.1	-
O	1.5	1.9	1.1	0.4	0.8	0.1
OH	5.0	5.0	2.4	2.4	2.7	1.4
H_2O	26.0	25.8	9.0	18.4	13.9	22.2
CF_3		-	e-11	0.02	e-12	0.3
CF_2		-	e-OS		e-08	-
CF	-	-	e-08		e-07	-
CF_2O	-	-	e-05	0.7	e-06	5.2
CFO	-	-	e-05	0.2	e-05	1.3
HF	-	-	36.0	24.9	27.7	16.9
CO	-	-	5.0	2.5	6.7	2.8
CO_2		-	4.1	3.2	2.6	0.2
Q (kJ/kg)	1741	1656	1811	2176	1979	2339
D (m/s)	1874	1830(a)	1875	1854(a)	1945	1922a

Experimental value

Table 4. Kinetic data used for the calculation of the induction times **(A,** frequency factor in cm^3/s mol; n, temperature exponent; **E„** activation energy in kcal/mol).

No.	Reaction			A	n	E_a
CF_3Br						
(5a)	$CF_3Br + H$	→	$CF_3 + HBr$	2.20e+14	0	9.45
CF_2HCl						
(5a)	$CF_2HCl + H$	→	$CF_2H + HCl$	4.65e+14	0	15.36
(5b)	$CF_2HCl + OH$	→	$CF_2Cl + H_2O$	1.28e+12	0	3.32
(5c)	$CF_2HCl + O$	→	$CF_2Cl + OH$	7.00e+12	0	8.58
CF_3H						
(5a)	$CF_3H + H$	→	$CF_3 + H_2$	1.16e+14	0	17.47
(5b)	$CF_3H + OH$	→	$CF_3 + H_2O$	2.65e+04	2.45	3.09
	$CF_3H + O$	→	$CF_3 + OH$	1.10e+12	0	3.19

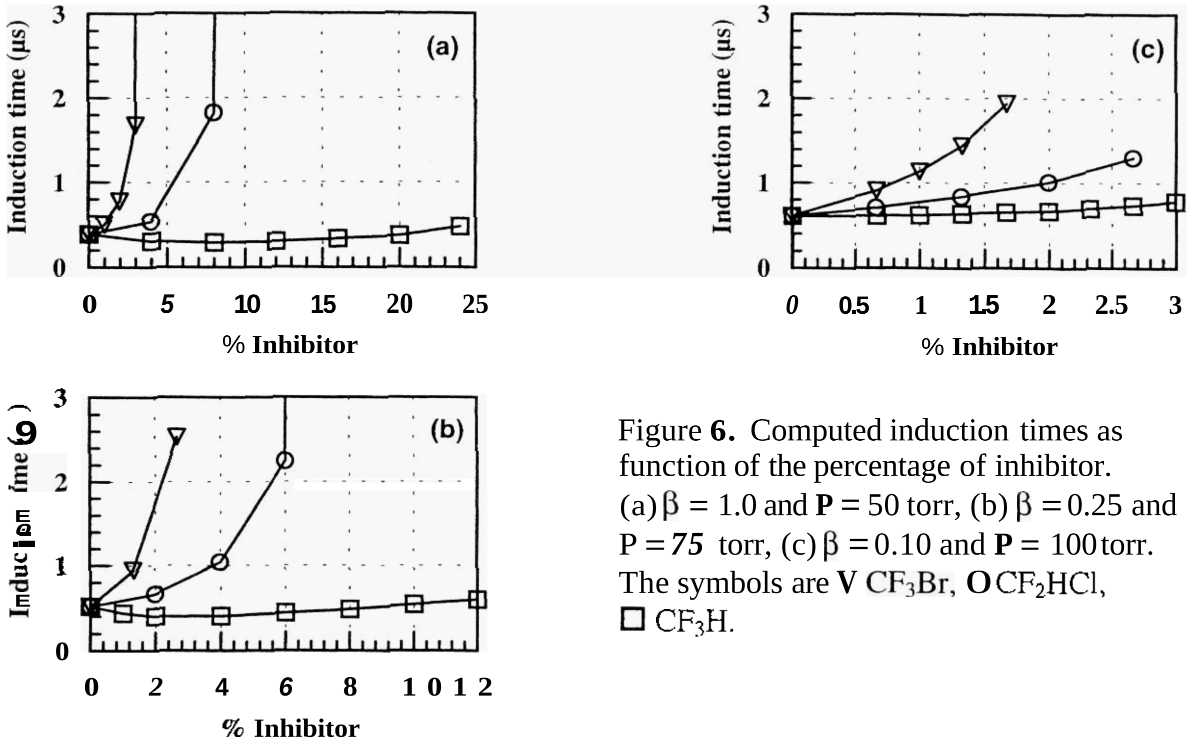

Figure **6.** Computed induction times as function of the percentage of inhibitor. (a) β = 1.0 and **P** = 50 torr, (b) β = 0.25 and P = 75 torr, (c) β = 0.10 and **P** = 100 torr. The symbols are **V** CF_3Br, **O** CF_2HCl, □ CF_3H.

detonation: the detonation fails due to a *chemical process*. In other terms, these two additives interfere chemically with the propagation mechanism of the detonation. Therefore, we can speculate that reaction (5c) is of minor importance for the first consumption of these species. However, compared to CF_3Br, larger amounts of CF_2HCl are required to increase the induction time and, close to extinction, the effect of its large heat capacity is not negligible anymore. On the other hand, the addition of CF_3H does not modify the induction time (Figure **6).** Moreover, large amounts of CF_3H (up to 25 %) are required to impede the detonation. Added in such large quantities, CF_3H acts as a thermal inhibitor through its large heat capacity and weakens the detonation through its large molar mass: the detonation fails due to a *physical process*. CF_3H does not interfere chemically to a significant extent with the overall detonation propagation mechanism. Therefore, we can speculate that reaction (5c) could play a more active role in the case of CF_3H, as demonstrated in flames studies by Richter et al. [17]. First conversion of CF_3H **by** O-atom could thus account for the promoting influence of CF_3H—and to some extent of CF_2HCl at low percentage—on the detonation. CF_2HCl corresponds thus to an intermediate case; it acts chemically and physically on the detonation.

7.0 CONCLUSIONS

Unexpected behavior of detonations in mixtures containing variable amounts of CF_4 and CF_3H has been observed, and some promoting influence of both additives is noticeable up to 10%. Such an influence can not be explained by the thermodynamic approach of the classical Chapman-Jouguet model. **A** chemical kinetics approach is necessary to understand the promoting or inhibiting behavior of the studied halogenated species.

When the additives mitigate and eventually extinguish the detonation wave, they act on the coupling process between the leading shock and the heat release zone by lengthening the induction zone, i.e., by behaving as radical scavengers. The type of primary attack of the added molecule by radicals is essential *to* provide an efficient inhibition: consumption of the additive by H radical is preferable to the one by OH, or O radicals. Reaction with O radicals might result in a slight promoting effect of the additive. This type of approach could be applied to more exothermic mixtures such as those studied by Moen et al. [18], and it accounts for the unusual behavior noticed on the critical diameter of C_2H_4 detonation with traces amount of inhibitors. The inhibiting power is also quite sensitive to the rate coefficient of the individual elementary inhibition reactions. The lower the hydrogen content in the fuel, the better the inhibiting action of the additive. A simple kinetic model has been developed to clarify the action of the primary attack by the additives. It provides a satisfactory approach and allows the macroscopic quantities (velocity, cell structure) to be related to the induction times. One of the difficult remaining issues is to collect reliable kinetic data on the primary decomposition of the halogenated compounds and their reactions with highly reactive radicals.

The experimental data collected in this work led to the following sequence of inhibition in increasing order of efficiency:

$$CF_3H < CF4 < C_2F_4H_2 \approx C_2F_5H < C_3F_8 < C_2F_4HCl \approx CF_2HCl < CF_3Cl$$
$$< CF_2Cl_2 < CFCl_3 < CF_2HBr < CF_3Br = CF_3I.$$

The nature of the halogen substituent plays a paramount role for the inhibition efficiency:

- Bromine and iodine containing compounds are the most efficient.
- CF_2HBr is slightly less active than CF_3Br because of the presence of the hydrogen in the additive.
- The inhibiting action of the chlorine containing species depends on the number of chlorine atoms in the additive.
- CF_4 and CF_3H have similar low efficiency.
- The presence of hydrogen atom(s) in the additive decreases the inhibition to some extent.
- The addition of molecules with a higher mass ($C_2F_4H_2$, C_2F_5H, C_3F_8, C_2F_4HCl) increases the overall specific heat and their inhibiting effect is mainly caused hy thermal dilution, i.e., a physical process.

In the series of investigated hydro-fluoro-chloro-alkanes, no real satisfactory substitutes of the trifluorobromomethane(CF_3Br or Halon 13B) are available to inhibit, or to extinguish efficiently gaseous detonations. Trifluoroiodomethane(CF_3I) acts as efficiently as Halon 13B.

As a conclusion, the bromine or iodine atom seems to be necessary to induce a real chemical inhibition mechanism of the gaseous detonations. Large amounts of other additives are required to achieve a similar influence on the detonation wave by acting as thermal diluent. This conclusion is particularly valid for mixture with fuels containing large amount of hydrogen (see mixtures #1 and 2). However, the influence of inhibitors on detonations can vary according to the nature of the fuel in the investigated mixtures. In hydrocarbon fuels the efficiency of the additive is rather small as demonstrated by Moen et al. [18]. It was confirmed also by the observations made in shock tube experiments [19,20]. But, for detonations propagating in acetylene mixtures the occurrence of trace inhibitors in the fresh gases mixture decreases the cell length, whereas at the incipient stage of a detonation, the onset of the detonation phenomena is delayed. The delays are the longer the higher the CF_3Br concentration. Those data have been discussed at length in a previous paper by Vandermeiren and Van Tiggelen [21]. Nevertheless, the action of an inhibitor during the transition from deflagration to detonation is practically nonexistent as noticed by Nzeyimana et al. [22].

8.0 ACKNOWLEDGMENTS

We thank Drs. F. Evariste and E. Nzeyimana for useful discussions about the role of halocompounds on detonation. We acknowledge also the financial support of NATO under contract 5-2-05 RG-890922 and of the European Union under contract EV5V-CT92-0230.

9.0 REFERENCES

1. H. Richter, P. Rocteur, J. Vandooren ,and P.J. Van Tiggelen (1995), "Flame Inhibition of Current Fire Extinguishers and of Potential Substitutes," *ACS Symposium Series 611 Halon Replacements Technology and Science,* Editors A.W. Miziolek and W. Tsang, pp. 304-320.
2. T. Noto, V. Babushok, A. Hamins, and W. Tsang, "Inhibition Effectiveness of Halogenated Compounds," *Combust. Flame* 112, pp. 147-160.
3. **R.** Strehlow (1988). *Combustion Fundamentals,* Mc Graw Hill, New York, NY.
4. W. Ficket and W.C. Davis (1979), *Detonation,* University of California Press, Berkeley, CA.
5. J.C. Libouton, M. Dormal, and P.J. Van Tiggelen (1975). "The Role of Chemical Kinetics on Structure of Detonation Waves," *15th Symp. Int'l on Combustion,* pp.79-86, The Combustion Institute, Pittsburgh, PA.
6. M.H. Lefebvre, E. Nzeyimana, and P.J. Van Tiggelen (1993), "Influence of Fluorocarbons on H_2-O_2-Ar Detonation: Experiments and Modeling," *Progress in Astro. and Aero.*, Vol. 153, pp. 144-161.
7. M.H. Lefebvre, B. Vanderstraeten, and P.J. Van Tiggelen (1995), "Modeling of Gas Phase Detonation in Complex Reactive Systems," *Shock Waves,* 4, pp. 271-276.
8. E.S. Oran, J.P. Boris, T. Young, M. Flanigan, T. Burks, and M. Picone (1981), "Numerical Simulations of Detonations in Hydrogen Air and Methane Air Mixtures," *18th Symposium Int'l on Combustion,* The Combustion Institute, Pittsburgh, PA, pp. 1641-1649.
9. S. Taki and T. Fujiwara (1978), "Numerical Analysis of Two-Dimensional Nonsteady Detonations," *AIAA Journal,* Vol. 16, pp. 73-77.
10. M.H. Lefebvre, E.S. Oran, K. Kalaisanath, and P.J. Van Tiggelen (1993). 'Simulation of Cellular Structure in a Detonation Wave," *Progress in Astro. and Aero.,* Vol. 153, pp. 64-71.
11. J.C. Libouton and P.J. Van Tiggelen (1976), "Influence de la composition du melange gazeux sur la structure des ondes de detonation," *Acta Astronautica*, Vol. 3, pp. 759-769.
12. F. Evariste, M.H. Lefebvre, and P.J. Van Tiggelen (1996), "Inhibition of Detonation with Halocompounds," *Shock Waves,* 6, 233-239
13. E. Nzeyimana and P.J. Van Tiggelen (1991), "Influence of Tetrafluoromethane on Hydrogen-Oxygen-Argon Detonation," *Progress in Astro. and Aero.,* Vol. 133, **pp.** 77-88.
14. F. Evariste and P.J. Van Tiggelen (1995), "Substitutes for Halons," *SUBSTHAL Final Report,* European Commission Programme in Environment. Contract N°EV5V-CT92-0230.

15. M.H. Lefebvre, F. Evariste, and P.J. Van Tiggelen (1996). Inhibition of $CO\text{-}H_2\text{-}O_2$ Detonations by Fluorocarbon Compounds, Proc. of the Joint Meeting of the Portuguese, Britsih, Spanish and Swedish Sections of the Combustion Institute, pp. 2261-2264.
16. M.H. Lefebvre (1992), PhD dissertation, Université Catholique de Louvain, Louvain La Neuve, Belgium.
17. H. Richter, J. Vandooren, and P.J. Van Tiggelen (1994), "Decay Mechanism of CF_3H, CF_2HCl in $H_2/O_2/Ar$ Flames," ***25th Symposium Int'l on Combustion,*** The Combustion Institute, Pittsburgh, pp. 825-831.
18. I.O. Moen, S.A. Ward, P.A. Thibaut, J.H. Lee, R. Knystautas, T. Dean, and C.K. Westbrook (1984), "The Influence of Diluents and Inhibitors on Detonations," ***20th Symposium Int'l on Combustion,*** The Combustion Institute, Pittsburgh, PA, pp. 1717-1725.
19. **Y.** Hidaka and M. Suga (1985), "Additive Effect of CF_3Cl on OH*, CH* and C_2* Emissions: Shock Tube Study with C2H4/O2/CF3Cl and H4/O2/CF3Cl Mixtures," ***Combust. Flame,*** 62, pp. 183-189.
20. A. Burcat, M. Dvinyaninov, and A. Lifshitz (1995), "The Effect of Halocarbons on Methane Ignition," ***Proceedings of 20th Int. Symp. on Shock Waves,*** Pasadena, CA.
21. M. Vandermeiren and P.J. Van Tiggelen (1988), "Role of an Inhibitor on the Onset of Gas Detonations in Acetylene Mixtures," ***Progress in Astronautics and Aeronautics,*** Vol. 114, pp. 186-200.
22. E. Nzeyimana, M. Vandermeiren, and P.J. Van Tiggelen (1986). "Influence of Chemical Composition on the Deflagration-Detonation Transition," ***Progress in Astro. and Aero.,*** Vol. 106, pp. 19-28.