Detonation Inhibition using Retardant Weight Analysis for Halogenated Compounds

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1. Introduction

Hydrogen explosions and detonations are of both practical and scientific interest. Hydrogen is used as a high-performance rocket fuel, appears in substantial quantities in the petroleum refining process, is formed in sufficient quantities in nuclear reactors, and has the potential to be a zero-emission fuel. From a scientific viewpoint, hydrogen fire and detonation suppression is an attractive area for study because the hydrogen combustion models are well-developed and quite simple. The hydrogen combustion mechanism is a critical part of all hydrocarbon combustion mechanisms; thus, any suppression mechanism that is effective against hydrogen may also be very effective against different hydrocarbon fuels. However, hydrogen also has a significant fire and explosion hazard [1-2]. Due to this, several methods, like venting, suppression, and inerting, are employed to reduce the hazards associated with hydrogen explosion or detonation. However, detonation suppression using inhibitors is the most effective method [3].

Halogenated compounds have been commonly used in studies as well as practical applications related to fire and detonation suppression and were found to be very effective inhibitors [4-7]. For years, halons have been the go-to suppressants in applications where excellent performance is required. The halons derive their unique fire suppression properties primarily from the catalytic action of the bromine atoms they contain. Bromine has been shown to participate in several catalytic chemical cycles that lead to the recombination of important combustion chain carriers, such as hydrogen atoms, to form stable species. However, halons are linked to the stratospheric ozone depletion problem. This has led to a ban on halon production under the Montreal Protocols on ozone-depleting substances [5].

In recent years, the research shifted towards finding a suitable halon replacement that is as efficient as CF_3Br along with less adverse effect on the environment. Several studies on detonation suppression have concluded that halogen-containing compounds are highly efficient in inhibiting gaseous detonations due to their combined physical and chemical effects [4-10]. However, studies in the past have focused mainly on selected halogenated inhibitors amongst the vast number of available halogenated compounds, especially in the case of detonation inhibition. Different classes of halogenated compounds, such as haloethenes, haloethanes, halomethanes, halogen acids, and compounds containing more than one halogen compound, may have different inhibition effectiveness based on their inhibition pathways, either chemical, physical, or both. Thus, it becomes imperative to evaluate the inhibition effect of prominent classes of halogen compounds and compare their performance to the CF_3Br. The

present study seeks to lay the basis for further research on different halogenated inhibitors and find a suitable replacement for Halon 1301.

In the present work, a numerical study is conducted to evaluate the inhibition effect of a series of halogenated inhibitors on hydrogen-air gaseous detonations. The halogenated compounds studied in the current work include halogen acids (HI, HBr, HCl, HF), halomethanes (CH_3I, CH_3Br, CH_3Cl, CH_3F), haloethenes (C_2H_3I, C_2H_3Br, C_2H_3Cl, C_2H_3F), haloethanes (C_2H_5I, C_2H_5Br, C_2H_5Cl, C_2H_5F), and complex halogenated compounds (CF_3I, CF_3Br, CF_3Cl, CF_4). The effect of the addition of these halogenated compounds on hydrogen-air detonation was studied using the one-dimensional ZND model with detailed chemistry. The inhibition effectiveness of inhibitors in gaseous detonations can be evaluated based on different detonation parameters [11]. In the current work, the inhibitors are ranked based on their ability to increase the detonation cell width calculated using the correlation with the induction length of a ZND detonation structure for stoichiometric hydrogen-air mixtures. The retardant weight required to suppress a detonation wave is also employed as a parameter to rank the different halogenated inhibitors. The lower (lean) and upper (rich) detonability limits for hydrogen-air mixtures were also computed with and without the halogenated inhibitors in the current work.

2. Numerical Methodology

ZND numerical computations in the current work were carried out to evaluate the inhibition effect of a series of halogenated compounds for stoichiometric H_2-air gaseous detonations. The modified version of CalTech Shock and Detonation Toolbox (SDT) [12], along with Cantera and MATLAB, was employed to simulate the ZND detonation structure. The HyChem model [13], which is based on the USC Mech II, was employed for the modeling of the high-temperature fuel oxidation chemistry. The chemical kinetics data of several halogenated inhibitors were taken from Westbrook et al. [4], and the reaction mechanism was updated with recent thermochemical data from the NIST database [14]. The kinetic data for the inhibitors investigated for the very first time was taken from the NIST database [14]. The details regarding the governing equations and the definition of the length and time scales can be found elsewhere [11].

The detonation cell width (λ) is the dominant detonation parameter and can be related to different detonation behaviors such as the critical ignition energy and the critical tube diameter, the geometric limit behavior, and the deflagration to detonation transition (DDT) length. Interestingly, over the years, it has been found that the induction length (Δ_i) of a ZND detonation structure co-relates directly to the detonation cell width (λ) of multidimensional detonations [15,16]. Thus, the prediction of the detonation cell width (λ) using different co-relations based on the induction length (Δ_i) of a ZND detonation structure has been widely adopted. In the current work, the detonation cell width (λ) was evaluated based on the recently developed co-relation of Crane et al. ($\lambda = 27.6\Delta_i$) [16]. It should be noted that smaller detonation cell sizes represent a strong and robust detonation wave and vice versa.

3. Results and Discussions

The primary suppression mechanism for halogenated compounds is the catalytic action of the halogen atmos. Though the inhibition mechanism for different series of retardants is different, they commonly reduce the concentration of active radicals (H, OH, O) in the reaction pool and thus slow down the chain branching reactions. The presence of these active radicals in the radical pool enhances the chemical kinetic rate of the branching reactions. The two important reactions primarily responsible for increasing the number of these chain carriers in the reaction pool of any hydrocarbon or hydrogen combustion with oxidizer are given below,

$$H + O_2 \rightarrow O + OH \qquad\qquad\qquad\qquad (R1)$$
$$O + H_2 \rightarrow OH + O \qquad\qquad\qquad\qquad (R2)$$

The addition of halogenated retardants to the reactant mixture consumes these radicals by undergoing a definite set of chemical reaction pathways. For example, the addition of halogen acids (HCl, HBr, HI, HF) results in H abstraction from the radical pool through the reactions R3-R6, where X in the reaction represents one of the halogen atoms (Cl, Br, F, I). Reactions R3, R4, and R6 are the recombination reactions in which the more active radical H is consumed, resulting in the formation of stable compounds and thereby depleting the concentration of H-radicals in the reaction zone.

$$H + HX \rightarrow H_2 + X \tag{R3}$$
$$H + X_2 \rightarrow HX + X \tag{R4}$$
$$X + X + M \rightarrow X_2 + M \tag{R5}$$
$$H + X + M \rightarrow HX + M \tag{R6}$$

Similarly, the halogenated hydrocarbon inhibitors deplete the radical pool through the reaction cycle R7-R10. In the reactions R7-R10, R denotes the vinyl, ethyl, or methyl group.

$$H + RX \rightarrow HX + R \tag{R7}$$
$$R + X_2 \rightarrow RX + X \tag{R8}$$
$$H + HX \rightarrow H_2 + X \tag{R9}$$
$$X + X + M \rightarrow X_2 + M \tag{R10}$$

Furthermore, the inhibition efficiency of these compounds varies, depending on which halogen atom is present in the retardant. The magnitude of the bond energy of the H-X and R-X bonds where X is the halogen atoms (F, Br, I, Cl) also determines the effectiveness of halogenated retardants in inhibiting detonation.

Detonation cell width analysis

The variation in detonation cell width with the retardant concentration for H_2-air mixtures at $P_0 = 1$ atm and $T_0 = 298$ K has been evaluated and illustrated in Figure 1. The detonability of a given fuel-air mixture decreases with increasing retardant concentration. The detonation cell width increases as the molar concentration of the retardants increases in the reactant mixture. At low concentrations, it can be observed that the addition of HI resulted in the largest increase in the detonation cell width, as shown in Figure 1. HI seems to exhibit a higher inhibition effect than other series of inhibitors at lower concentrations up to 10000 ppmv.
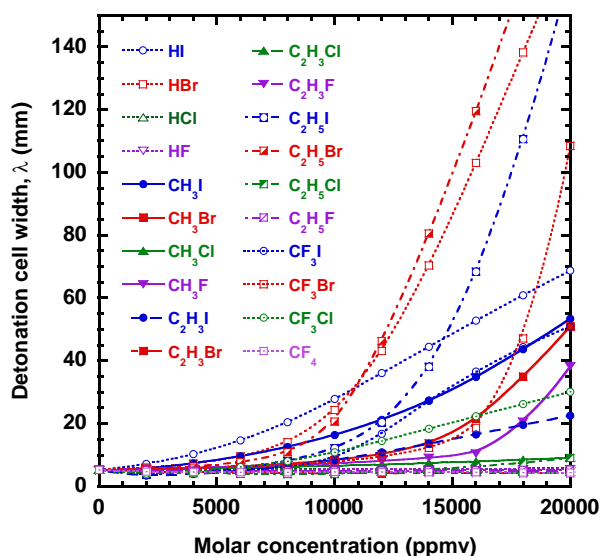

Figure 1: Variation in the detonation cell width ($\lambda = 27.6\Delta_i$) with the concentration of retardants for stoichiometric H_2-air mixture at $P_0 = 1$atm and $T_0 = 298$ K.

However, after that, a significant increase in the detonation cell width can be observed in the case of inhibition with C_2H_5Br, HBr, and C_2H_5I additives. Figure 1 shows that the detonation cell width increases more for CF_3Br when compared to CH_3Br in the range of molar concentrations of 17000 ppmv to 20000 ppmv. It indicates the inhibition effect due to additional fluorine atoms in CF_3Br. It was observed that the detonation cell width first decreases for smaller concentrations of inhibitors such as CF_3Cl, CF_3I, C_2H_3I, and C_2H_5I (refer to Figure 1), where a local minimum in the detonation cell width was observed for such inhibitors at lower concentrations. It suggests that the addition of these retardants to H_2-air explosive mixtures at lower concentrations has a promotion effect on the resulting detonation structure as it reduces the detonation cell width.

In the current work, bromine-containing species were found to possess the best inhibition efficiency, with fluorine-containing inhibitors being the least efficient, as evaluated by the cell width analysis.

Retardant weight analysis

A self-sustained detonation wave has a coupled reaction zone and the leading shock, propagating by the mechanism of periodic reignition. The addition of inhibitors to the fuel-oxidizer mixture generally delays the production of chain carriers and increases the induction length of the detonation. A dramatic increase in induction or reaction zone length at a higher concentration of inhibitors could decouple the reaction zone from the leading shock front and transform a self-sustained detonation into a loosely coupled shock flame complex. On a more fundamental level, the reaction zone, in such cases, increases in thickness and eventually decouples from the leading shock front. In such scenarios, the underlying detonation wave attenuates and degenerates into a deflagration wave. Therefore, the efficiency of different series of inhibitors could also be evaluated based on the amount of retardant (in kg) required to attenuate the detonation.

Table 1: Calculation of retardant weight required to attenuate the detonation of stoichiometric H_2-air mixture at pressure and temperature of 1 atm and 298 K, respectively.

Fuel-Ox	Retardant (retd)	X_{H_2}	X_{air}	X_{retd} required for inhibition	Y_{retd} (%)	Retardant weight[b] (kg)	Δ_i (m)
	C_2H_5F	0.26	0.62	0.12	0.24	45.14	0.246
	CH_3F	0.23	0.55	0.21	0.31	62.26	0.304
	CH_3Cl	0.25	0.59	0.17	0.33	69.41	0.293
	C_2H_5Br	0.27	0.64	0.09	0.34	73.74	0.285
	C_2H_5I	0.27	0.65	0.07	0.37	81.80	0.274
	C_2H_3F	0.23	0.54	0.23	0.40	94.02	0.234
	CH_3Br	0.24	0.57	0.19	0.51	147.62	0.264
	CF_3I	0.26	0.63	0.11	0.52	155.36	0.162
$H_2 - air$[a]	C_2H_3Cl	0.21	0.51	0.28	0.54	163.47	0.201
	CF_4	0.22	0.53	0.24	0.57	188.89	0.191
	CF_3Br	0.25	0.59	0.16	0.58	196.03	0.205
	CH_3I	0.24	0.58	0.17	0.59	202.13	0.108
	HF	0.12	0.28	0.60	0.59	205.46	0.334
	C_2H_3Br	0.23	0.54	0.23	0.61	219.63	0.198
	C_2H_3I	0.24	0.57	0.20	0.64	252.10	0.103
	HBr	0.17	0.41	0.41	0.73	383.24	0.263
	HCl	0.11	0.26	0.63	0.75	417.87	0.273
	HI	0.19	0.45	0.36	0.77	486.38	0.454

[a]1 mole of air ~ 1 mole of O_2 + 3.76 mole of N_2.

bRetardant weight was calculated for 4 kg of hydrogen and 137.2 kg of air for H_2 – air mixtures.

The retardant weight for an inhibitor is calculated based on the molar concentration of the inhibitor (when added to a stoichiometric H_2-air mixture), at which no peak in thermicity is observed. Based on the ZND computations, the weight of retardants required to attenuate a stoichiometric H_2-air detonation is presented in Table 1. The retardant weight was calculated corresponding to the stoichiometric H_2-air mixture, where for 4 kg of H_2, 137.28 kg of air is required for complete combustion.

Halogen acids were found to be the least effective inhibitors among all the classes of halogenated inhibitors based on the retardant weight analysis. Among all the inhibitors studied in the current work, HI (486 kg) required the largest retardant weight to attenuate a stoichiometric H_2-air detonation which was found to be more than 1000% than that required by C_2H_5F (45 kg), the most effective inhibitor.

Detonability limits of H_2-air-retardant mixtures

The detonability limits effectively describe the range of equivalence ratio over which a hydrogen-air mixture can sustain a self-propagating detonation wave. The detonability limits are inherently important for propulsive applications (RDEs and PDEs) as well as for safety and hazard prevention. In the case of propulsive applications, the aim is to increase the range of equivalence ratios that can sustain a detonation wave or, in other words, increase the detonability of a given combustible mixture. While in the case of safety and hazard prevention applications, the motivation is to reduce the range of equivalence ratio over which a self-propagating detonation can be sustained. Thus, the lean (lower) and the rich (upper) detonability limits of H_2-air mixtures were computed in the presence of halogenated inhibitors (20000 ppmv), and the results are reported in Figure 2. The ZND computations for the detonability limits were carried out at an initial pressure, $P_0 = 1$ atm, and initial temperature, $T_0 = 298$ K.
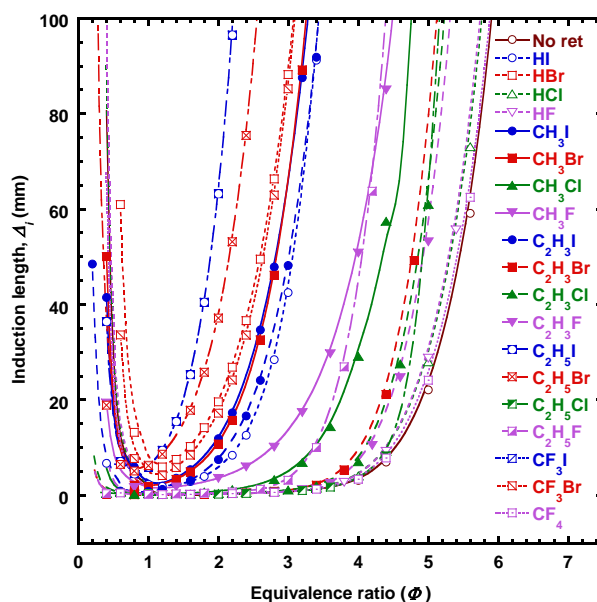

Figure 2: Variation in induction length with the equivalence ratio with and without 20000 ppmv of the retardants for H_2-air mixtures at $P_0 = 1$atm and $T_0 = 298$ K.

The detonability limit curves shrink in the presence of halogenated inhibitors in most of the cases with few exceptions, as can be seen in Figure 2. The lower (φ_L) and upper (φ_R) detonability limits of hydrogen-air mixtures are significantly affected with the addition of the halogenated inhibitors (at 20000 ppmv) except for CF_4, in which the limits are minimally affected. Among all the inhibitors studied in the present work, the maximum reduction in the rich detonability limit (φ_R) can be observed for C_2H_5I, where φ_R reduces from $\varphi_R = 7.17$ (no diluent) to $\varphi_R = 2.96$ (20000 ppmv of C_2H_5I). Similarly, in the case

of the lean detonability limit (φ_L), the maximum change in φ_L was observed for HBr, where φ_L changes from $\varphi_L = 0.36$ (no diluent) to $\varphi_L = 0.46$ (20000 ppmv of HBr).

4. Conclusions

The inhibition efficiency of a series of halogenated inhibitors for stoichiometric H_2-air gaseous detonation has been evaluated in the current work. The inhibition effectiveness based on the retardant weight is a result of the active radical scavenging by the halogen radicals and the molecular weight of the inhibitor. Fluorinated inhibitors were found to be the best inhibitors, followed by chlorinated, brominated, and iodinated inhibitors for all the classes of halogenated inhibitors except the complex halogenated hydrocarbon inhibitors, where CF_3I showed the highest inhibition effect. The inhibitors ranking based on the hydrocarbon class is given below,

Ethyl halides (C_2H_5X) > Methyl halides (CH_3X) > Vinyl halides (C_2H_3X) > Trifluoromethyl halides (CF_3X) > Halogen acids (HX)

The lean (φ_L) and the rich (φ_R) detonability limits of hydrogen-air mixtures are considerably affected by the addition of the halogenated inhibitors (HX, CH_3X, C_2H_3X, C_2H_5X, CF_3X). The computations showed that the detonability limits were reduced in the presence of halogen acids and complex hydrocarbon inhibitors, with few exceptions. However, in the case of hydrocarbon inhibitors, φ_R was reduced for all the inhibitors, but φ_L was found to be lower than the no-diluent case indicating an increase in the range of equivalence ratio over which hydrogen-air mixtures can sustain a self-propagating detonation wave. Among all the inhibitors, the maximum change in φ_R and φ_L was observed for C_2H_5I and HBr, respectively.

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