SIMULATION STUDIES OF THE INFLUENCE OF FLUORINE AND BROMINE CONTAINING FIRE SUPPRESSANTS ON IGNITION BEHAVIOR

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Abstract

The effect of a number of possible flame suppressants: Br_2, HBr, CH_3Br, CF_3Br, CF_3H, CF_2H_2, CF_4, C_2F_6, C_2HF_5 and $C_2H_2F_4$, on the ignition behavior, as represented by the ignition delay, of a variety of combustible gases: H_2, CH_4, CH_3OH, and C_2H_6 with air at temperatures between 900-2000 K, 0.5-1.5 atm, equivalence ratios of 0.5-1.3 and additive concentrations ranging from 0-30% by volume are described on the basis of computer simulations. Wherever possible comparisons were made with experimental results and in general fits were quite satisfactory. The presence of additives can lead to a full range of phenomena: ranging at the highest temperatures in methane oxidation, from promotion of combustion as evidenced by decreased ignition times to the more expected situation at less severe condition where ignition times are significantly lengthened. Aside from pure ignition behavior we also noted at higher concentrations of inhibitors overall change in the heat release rates. The chemical action of these compounds on combustion properties is very complex and cannot be attributed to a single type of chemical reaction. The observations are interpreted in the context of the creation and destruction of active radical species as a result of the presence of fluorine and bromine species. A number of mechanistic possibilities that control the results are considered. The simulation results are clearly incompatible with a purely physical or heat capacity mode of flame suppression. An attempt to use the simulation results to give a rank ordering of the inhibitive powers of the various agents will be discussed.

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Introduction

The inhibition and extinction of combustion processes is of great practical importance. Currently, there is much interest in finding alternative flame retardant compounds that do not deplete ozone. More generally, the analysis of inhibition mechanisms leads to the possibility of better understanding of the limiting behavior of combustion systems and therebye controlling combustion behavior. Much of the present knowledge on inhibition is empirical[1-4]. There are many details that are still unclear and there is no real understanding of how inhibition effects a wide range of combustion phenomena.

Certain halogenated compounds are widely used as fire suppresants and bromine compounds such as CF_3Br (Halon 1301) are known to be the most effective. In the related area, hydrocarbon oxidation, the situation is not straightforward. Flame speeds are reduced and limits of inflammability are narrowed with addition of inhibitors. On the other hand hydrogen bromide is a promoter for the slow oxidation of hydrocarbons[4-5]. There exists a surprisingly large amount of data indicating that many flame inhibitors may promote combustion processes. Some of these are: slow combustion, ignition, spontaneous combustion, reaction behind shock waves and detonation[5-17]. It appears that the nature of the additives, the regime of combustion, initial concentration of the additives and other initial conditions can lead to either inhibition or promotion.

This is a preliminary report on simulation studies aimed at defining the ignition behavior of combustible mixtures in the presence and absence of inhibitors. The influence of the additives: HBr, Br_2, CH_3Br, CF_3Br, CH_2F_2, CHF_3, CF_4, C_2F_6, C_2HF_5, $C_2H_2F_4$, on the ignition behavior of mixtures of methane, ethane, methanol and hydrogen, respectively, with air at temperatures 900-2000 , pressure of 0.5-1.5 atm equivalence ratio 0.5-1.3, and additive concentration 0-30% by volume have been studied.

Modeling Techniques and Kinetics Data Base

The main property determined from the simulation studies was the ignition delay. Ignition delay was characterized in terms of the following times: (1) time of achievement of maximum concentration of OH, (2) time for temperature rise of $100^{o}K$, (3) time of steep increase of temperature and changing of concentration of initial reactants and (4) time for increase in temperature for one characteristic temperature rise (RT^2/E) where E is the global activation energy. The uncertainty in the calculated ignition delays, from such determinations ranges between 10-30%. The limits to such studies arise at high temperatures where the reaction time is comparable to ignition delay. Calculations were carried out using the Sandia Chemkin Code SENKIN and analyzed with an NIST Interactive Graphics post processor. The model that is used is that of a plug reactor at constant pressure. This also corresponds directly to the ignition behavior behind shock waves.

The kinetic data base consists of three distinct sets of reactions. They are the reactions of importance in hydrocarbon oxidation (C_1-C_2), the C/H/O reaction subset. Second, the data base containing fluorocarbon chemistry or the C/H/O/F subset. Finally, the reactions with added bromine compounds or the C/H/O/F/Br subset. The entire model includes about 900 reactions with 100 species. No claim is made about the absolute correctness of the rate constants. Work is still proceeding on revising and updating the data base. Many new reactions have been added and the values of older rate constants have been brought up to date. For comparison we carried calculations using the data base of Westbrook[18].

The C/H/O reaction set is based on the models of Miller and Bowman[19] and Egolfopoulos et al[20]. Some of the rate constants have been adjusted on the basis of review of Tsang[21] and Baulch et al[23] and brought up to date using the NIST data base[24]. We have added into the data base reactions involving the formation and consumption of CH3O2 and CH3OOH. Adjustments of the rate constants were made in order to match existing experimental results on ignition delay times and kinetics studies on the oxidation of hydrogen, methane, formaldehyde, methanol[9-14,25,26]. The simulations are validated on the basis of the experiments summarized in Table 1.

The C/H/O/F set of reactions was derived from the work of Westmoreland[27] and the NIST report[28]. This contains a detailed kinetic mechanism involving C_1 and C_2 fluorinated hydrocarbons of importance in flame suppression. An important difference in this scheme in comparison to that of Westbrook[18] is the treatment of the reaction of CF_3+O_2. Westbrook favors the formation of CF_2O and OF, while the NIST work[28] and the analysis of Vedenev[29] favors the formation of CF_3O and O. In this form, the reaction is a branching process while the mechanism of Westbrook ultimately leads to termination. The results of Vedenev and NIST are determined through transition state calculations. The former leads to much larger decreases in ignition delay than would be warranted from experimental results. The NIST values are in better accord with experiments and are based on more recent thermochemistry. Thus the basis for estimating transition state properties are probably more accurate. The NIST expression $2.46 \times 10^{13} \exp(-12000/T)$ $cm^3 mol^{-1} s^{-1}$ in used in our simulations.

The set of reactions containing bromine species was based on the mechanisms of Westbrook[18]. We have updated the data base by adjusting the rate expressions to reflect more recent measurements. Some of these changes are as much as an order of magnitude. Westbrook's reaction set is a very abbreviated one. He assummed that because of the difference in the energy of C-H and C-Br bonds in the CH_3Br molecule, the bromine atom will always be abstracted first. Br atoms can be abstracted only by H and Br and not any other reactive species. The first assumption mean that species such as CH_2Br and CHBr can be ommitted. The second assumption is made primarily to avoid species such as BrO and BrOH. We have considered reactions involving BrO, BrOH, CH_2Br and the constants were estimated by comparable reactions with Cl species. Effects were approximately 30% at low temperatures for 1% of additive and at higher temperatures effects were much smaller. Actually with our more complete C/H/O/F mechanism we should be considering a much larger set of reactions. We are in the process of doing this. However the preliminary results mentioned here suggest that the Westbrook mechanism is fairly robust and that the important phenomena have been captured.

Comparisons with Experimental Data

Table 1 contains a summary of experimental measurements with which we have made comparisons with our model. This includes not only ignition delay but also species concentration as a function of time. Agreement is better than a factor of 2. This is not a complete validation of all the rate constants we have used. It is suggestive of the validity of the results derived from such calculations. There must be some cancellation of errors. The important point is that the main physical characteristics of the system are reproduced with reasonable accuracy.

Results and Discussion

Figure 1 contains results on the dependence of the ignition delay for methane, methanol, ethane and hydrogen with air in stochiometric mixtures at an atmosphere pressure and 1% CF_3Br. It is clear that a variety of behaviors are possible and that depending on the fuel and temperature CF_3Br can act as a promoter or inhibitor. Suzuki[10] has observed such promotion effects for CF_3Br and CF_3H in methane from his shock tube study. For ethane they found inhibition and this was in fact reproduced and used for validating our mechanism. The results of Reid[25] and Hertzberg[26] lead to ignition delay times of 10-30 secs at 900K for stochiometric methane mixtures at 1 atm without CF_3Br. This can be compared with the calculated results from Westbrook's[18] model of 31 seconds. Our results yield a value of 13 seconds. Westbrook's model gives below 1100 K with 1 % CF3Br inhibition but at higher temperatures promotion occurs. From our model promotion occurs across the whole range. Thus the present results and those of Westbrook's model span the experimental observations.

Figure 2 contains the results of simulations with variations of equivalence ratio ranging from 0.5 to 1.3 at 1 atm and temperatures 900 and 1500 K in the presence of 1% CF_3Br for methane and hydrogen. For methane we also calculated results with CF_3H as an additive. Decrease in equivalence ratio leads to decreasing ignition delay for pure mixtures. For H_2 at 1500K the ignition delay is weakly dependent on the equivalence ratio. In the case of H_2 at 900 K and methane at 1500 K the general trends of increasing ignition time with equivalence ratio is similar with or without additive. There is of course a difference in the absolute magnitudes. It is interesting in the latter case the effect of CF_3H and CF_3Br are equivalent. For methane at 900 K the effect of CF_3Br is to increase the ignition delay at low equivalence ratio. The ignition delay then decreases to values and dependences similar to the other results. For the pure compounds and in the presence of CF3Br our results are in agreement with that for Westbrook's model except that our values are again somewhat lower.

Results of calculations for CH_4 and H_2 for stochiometric mixtures and pressure ranges of 0.5 to 1.5 atms can be found in Figure 3. For pure methane under all conditions the ignition delay decrease with pressure. This follows the general trend derived from Westbrook's model. However when CF3Br is added, Westbrook's model leads to inhibition and we find promotion. Westbrook's model also leads to increased inhibition with pressure. In our calculations at the highest pressures the effect of additive decreases. For stochiometric H_2 and an initial temperature of 900K the character of the dependence of the ignition delay on pressure is different. Ignition delay of H_2 mixture with air with additive sharply increases with increasing pressure. This is because the initial condition of the system is near the extended 2nd explosion limit. The effect of pressure is to pass this limit where we go to lesser degree of branching. A consequence of this is that CF_3Br inhibits the process at lower pressures. With increasing pressure inhibition changes into promotion.

The results of our simulation on stochiometric mixtures of methane and H2 with varying quantities of CF_3Br and CF_3H can be found in Figure 4. The change is non-monotonic. Curves for methanol are similar to that for methane. Initially, ignition delay is decreased. At concentrations 0.5 to 2% there is an optimum concentration for promotion. Subsequently, there is a continual increase in the ignition delay. This is connected with a decrease in heat release rate and is most likely due to the pyrolysis of the additive. Using Westbrook's model[18], during the oxidation of methane, inhibition occurs at concentrations of CF_3Br as low as 0.1%. When concentration was increased, there was a decrease in igniton delay followed by increase at 5% or greater. This is a demonstration of the differences in chemistry that was used in the models.

The increase in ignition delays at large concentration is very sharp. The critical concentration is 10-30% by volume. This general phenomena has been observed by Gmurcyk in the case of processes occurring in the quasi-detonation regime in ethylene-air mixtures with inhibitors such as CF_3Br and CF_3H[17]. It is connected with an unexpected decrease in the temperature (as large as 200 degrees) in the course of explosion. This decrease in temperature leads to a slower rate of reaction. We have not noted any mention of this phenomena in the literature. This may be due to the fact that experiments have not usually carried out with such high additive concentrations. The general phenomena can be easily understood in terms of the onset of an endothermic reaction with a large activation energy which is not activated until high temperatures are reached.

Discussion

A wide variety of mechanisms has been proposed as explanations for inhibition. These include scavenging of active chain carriers, thermal effects (from cooling and dilution), catalytic combination of chain carriers, etc[1-4]. An interesting observation from the literature is the necessity for concentrations of additives (the peak percentage concentration) near that of the fuel for extinguishment. For example in the case of a stochiometric mixture containing 9.5 % methane, the concentration of CF_3Br necessary for extinction, from a variety of sources range from 2-9%[1]. In the case of propane, a 4% stochiometry mixture requires 3-5% of CF_3Br[1]. At such large concentrations it is necessary to consider the coupling of agent and fuel destruction mechanisms. Large concentration of inhibitors generates, by themselves thermal effects through reactions proceeding along endothermic decomposition pathways. The endothermic decomposition products may be less chemically active and this becomes a form of chemical inhibition through changes in reaction pathways and distribution of products. For CF_3Br the transient products are CH_3Br, CF_3H and CF_2O. The data base used in the simulations may not suffciently accurate for the simulation of such behavior. There is need for much more work in this area and some of this work is currently being carried out.

Table 2 contains a summary of simulation results on the inhibitive and promotion characteristics for a variety of additives in methane, methanol, hydrogen and ethane. The rankings are based on an inhibitor or promotion efficiency, ϵ , which is the ratio of ignition delays with or without additives and vice versa for promotion. The results are based on 1% additive with initial temperatures of 900K, stochiometric mixtures and 1 atm pressure. The efficiency is variable and depends on the reaction system, initial conditions and concentration of additives. At the 1% level, the maximum inhibitive action is observed for H_2 oxidation with HBr and has the value of 4.6. The maximum promotion effect for CF_3Br in methane is a factor 1.9. It is interesting that there seem to be very little effect in promotion or inhibition with methanol and is in agreement with experiments. For ethane at 900 K all additives leads to promotion. Temperature increase changes the mode of action and at 1500 K all additives inhibit ignition.

Conclusions

a. From simulation results we showed that additives can promote as well as inhibit depending on the reaction conditions. Ignition delay is therefore not a good measure of inhibitive efficiency.

b. The dependence of delay on concentration has very complex behavior. Large effects appear only with large concentrations. Rapid temperature increases are stopped and is due to the characeteristic time of endothermic decomposition of the additives.

c. We suggest work on coupling mechanisms for combustion and suppression. This involves a detailed study of reaction pathways, particularly to less reactive and endothermic substances.

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Table 1: Experimental results used to calibrate data base

Reaction system	Experimental setup initial conditions	Parameters for comparison	Ref
CH_4+air	static reactor, 900K, 1 atm	ignition delay	25,26
CH_4+O_2+Ar	shock wave,1400-2100K, 1.5-3.5 atm	ignition delay	10,11
$CH_4+O_2+CF_3H+Ar$	"	"	10
$CH_4+O_2+CH_3Br+Ar$	"	"	10
$C_2H_6+O_2+Ar$	"	"	10
$C_2H_6+O_2+CF_3Br+Ar$	"	"	10
$CH_2O+O_2+N_2$	flow reactor 943-995K, 1 atm	concentration history CH_2O, CO, H_2, O_2	30
H_2+O_2+Ar	shock wave,900-1660K, 5atm	ignition delay	31
$H_2+O_2+CF_3Br+Ar$	"	"	31
$CH_3OH+O_2+N_2$	flow reactor 1030 K, 1 atm	concentration history O_2,CO,H_2,CH_3OH,CO_2.CH_2O	32
$CH_3OH+O_2+N_2$	flow reactor 998 K 1 atm	concentration history CO, CH_3OH, H_2, CH_2O	33
$CH_3OH+O_2+N_2$	static reactor 823 K, .263 atm	concentration history CO,CH_3OH,H_2,CO_2,CH_2O	34
CH_3OH+O_2+Ar	shock wave, 1200-1700K 10^5-$2x10^{-4}$ mol/cm_3	ignition delay	35
CF_3Br+H_2+Ar	shock wave	concentration history product distribution CF_3Br,CF_3H,C_2F_6, C_2F_4	36

Table 2: Summary of results on ranking of compounds for promotion or inhibition at 1 atm and 1% additive [In]

System,initial condition		Inhibition	Promotion
CH_4,	900	$HBr>Br_2>C_2H_2F_4>CF_4>C_2F_6$, C_2HF_5(ϵ =1) $\epsilon_{i,max}=2.1$	$CF_3Br>CH_3Br$, $CHF_3>CH_2F_2$ $\epsilon_{p,max}=1.9$
	1300	$C_2H_2F_4>CF_4$ (ϵ =1) $>CHF_3>Br_2$, $HBr>C_2F_6$ $\epsilon_{i,max}=1.4$	$C_2HF_5>CH_2F_2>CF_3Br>CH_3Br$ $\epsilon_{p,max}=6.5$
	1700	$C_2H_2F_4>CF_4$(ϵ =1) $\epsilon_{i,max}=1.1$	C_2HF_5, $CH_2F_2>CH_3Br>CHF_3$, CF_3Br, $C_2F_6>Br_2>HBr$(ϵ_p=1) $\epsilon_{p,max}=4.9$
	900 [In]=20%	$Br_2>CHF_3$(ϵ =1.6) $>CF_4>C_2F_6>CH_2F_2$ $\epsilon_{i,max}=33$	$C_2H_2F_4>CH_3Br$(ϵ =2) $>C_2HF_5>HBr>CF_3Br$ $\epsilon_{p,max}=19$
CH_3OH,	900	CF_4, CHF_3, C_2F_6, C_2HF_5, $C_2H_2F_4>CH_3Br$, CH_2F_2(ϵ =1) $\epsilon_{i,max}=1.03$	$HBr>Br_2>CF_3Br>CH_2F_2$(ϵ =1) $\epsilon_{p,max}=1.3$
H_2	900	$HBr>Br_2>CH_3Br$ $\epsilon_{i,max}=4.6$	$CF_3Br>CH_2F_2$, $C_2H_4>C_2HF_5>CHF_3>C_2F_6$, CF_4 (ϵ =1) $\epsilon_{p,max}=1.7$
	1300	$Br_2>Hbr>CH_3Br>C_2H_2F_4$, CF_4, CHF_3, CH_2F_2 (ϵ =1) $_{i,max}=6.2$	$CF_3Br>CF_5$, C_2F_6 (ϵ =1) $\epsilon_{p,max}=1.2$
	1700	$Br_2>HBr>CF_4$ (ϵ =1) $\epsilon_{i,max}=1.6$	$CF_3Br>C_2HF_5>C_2F_6>CH_3Br$, $CH_2F_2>CHF_3>C_2H_2F_4$ (ϵ=1) $\epsilon_{p,max}=2.3$
C_2H_6	900	C_2F_6, CF_4 (ϵ=1)	$CF_3Br>Br_2$, $HBr>CH_2F_2>CH_3Br>CHF_3$, $C_2H_2F_4$, C_2HF_5 (ϵ =1) $_{p,max}=1.4$
	1500	$Br_2>Hbr$, $CH_3Br>CF_3Br>CHF_3>C_2H_2F_4$) CH_2F_2, C_2HF_5, $C_2F_6>CF_4$ (ϵ = 1) $\epsilon_{i,max}=2.7$	

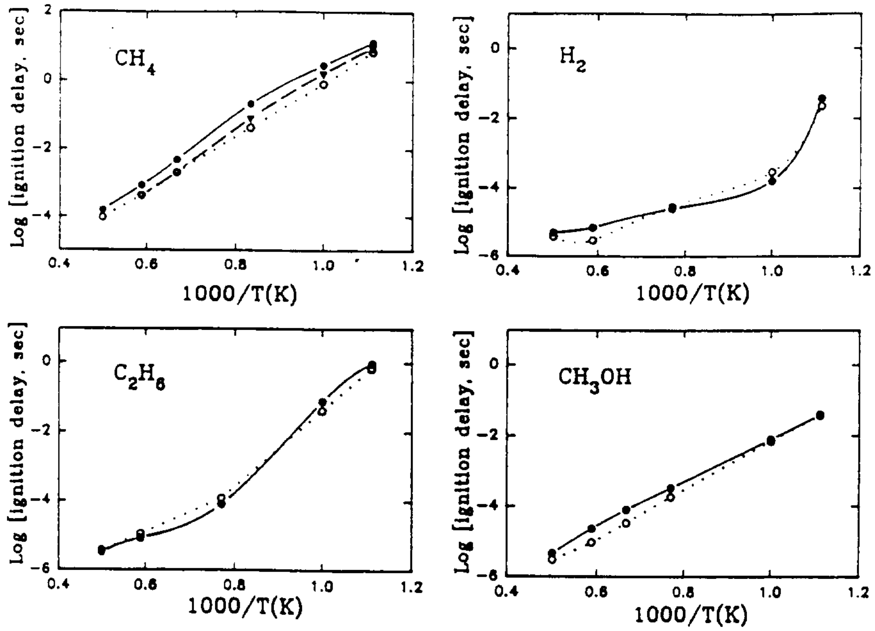

Figure 1. Temperature dependence of ignition delay in the presence (○) CF_3Br and (∇)CF_3H and absence (●) of additives for stochiometric mixtures of methane, hydrogen, ethane and methanol at 1 atm. Additives are at 1% level. Solid lines are for pure compounds. Dotted lines are from studies with additives.

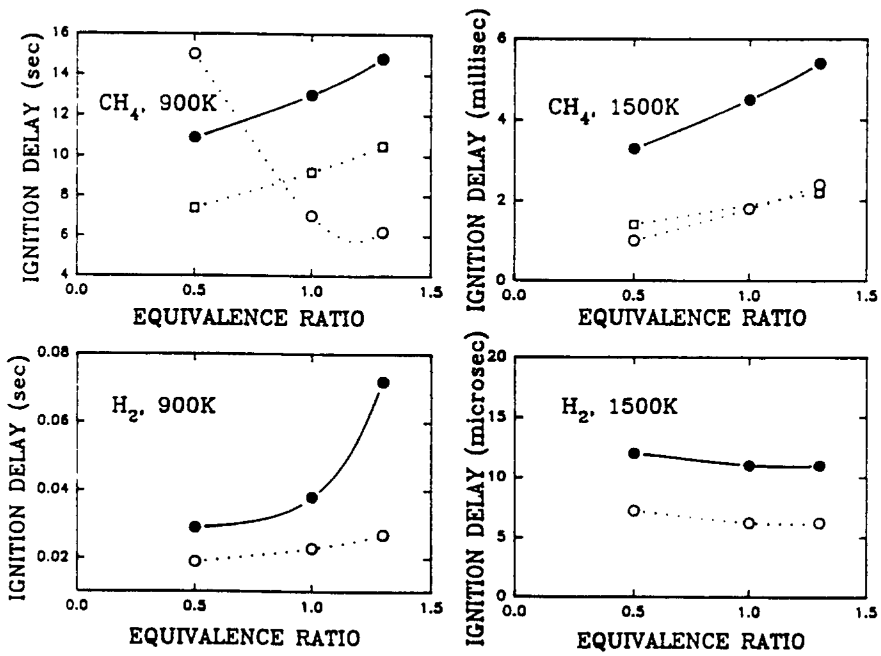

Figure 2. Dependence of ignition delay on equivalence ratio for stochiometric methane and hydrogen with (□)CF_3H, (○)CF_3Br and without (●) additives at 1 atm. Additives are at 1% level. Solid lines are for pure compounds. Dotted lines are from studies with additives.

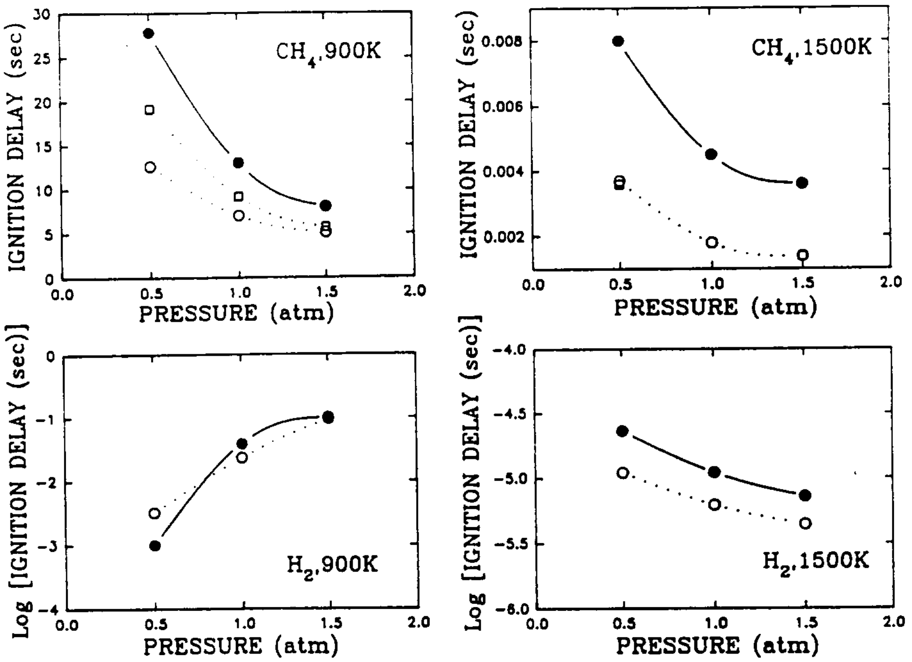

Figure 3. Dependence of ignition delay on pressure for stochiometic methane and hydrogen mixture with (○)CF_3Br and (□)CF_3H and without (●) additives. Additives are at 1% level. Solid lines are for pure compounds. Dotted lines are from studies with additives.

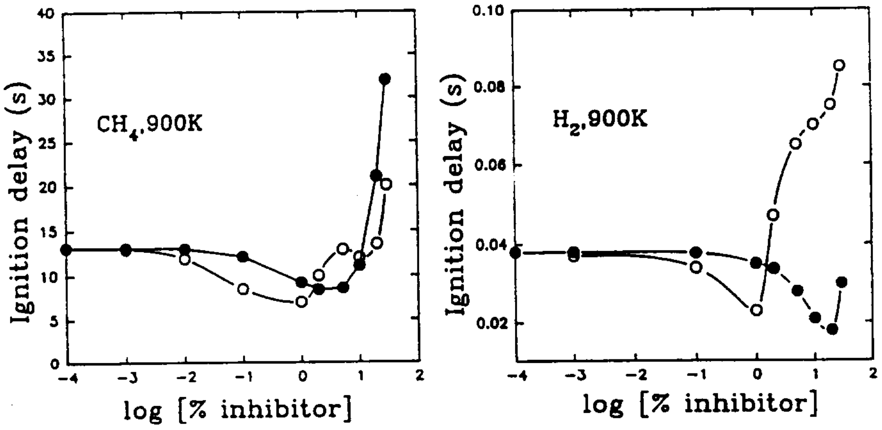

Figure 4. Dependence of ignition delay for stochiometric methane and ethane mixtures at 900 K at 1 atm as a function of added inhibitors (●)CF_3Br and (○)CF_3H.