A DETAILED CHEMICAL KINETIC MODELLING STUDY ON HIGH TEMPERATURE IGNITION OF METHANE / AIR MIXTURES DOPED WITH C_3F_7H

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ABSTRACT

C_3F_7H (FM-200) has recently been introduced as an alternative for Halon 1301 (CF_3Br) fire suppression agent. In this paper, as part of an effort to study the effects of C_3F_7H on high temperature ignition of gaseous fuels, we are expanding on our earlier evaluations of ignition inhibition characteristics of C_3F_7H. Of particular interest is a better or improved understanding of the fundamental mechanisms by which C_3F_7H functions as an inhibitor. We found that the ignition delay is primarily controlled by the initial C_3F_7H decomposition kinetics, which releases active species into the system. At low temperatures (below1000 K) these active species increase the overall reaction rate by initiating new chain reactions. However, at higher temperatures, due to competition between the main chain branching reaction of CH_4 combustion and reactions involving C_3F_7H derivatives (e.g., C_3F_7 and C_3F_6), the heat release rate of the overall combustion reaction is substantially decreased leading to a longer ignition delay time.

INTRODUCTION

Halon extinguishing agents exhibit remarkably good levels of flame suppression effectiveness because they extinguish fires primarily by chemical suppression mechanisms. However, halons are being phased out due to their ozone depletion potential (ODP). Based on the Montreal Protocol, the production of halon fire extinguishing agents in many countries ceased as of January, 1, **1994.** This created tremendous research efforts worldwide to develop appropriate replacements and alternatives. Over the past several years, a number of alternative agents have been introduced and subsequently commercialised. One of such new agents, is C_3F_7H or heptafluoropropane, which is also known by its trade name as FM-200.

A number of experimental studies have been conducted on the flame suppression effectiveness of C_3F_7H, and DiNenno [1] presents a good summary of these works. Only a few [2] theoretical studies (chemical kinetic analysis), however, have been conducted on this new fire suppression agent mainly because no reliable reaction mechanism has been available. The situation was changed recently when a new reaction mechanism for C_3F_7H was developed [3] and subsequently used to study the flame inhibition chemistry of C_3F_7H [4] and its toxicity [5] in typical room fires. The same reaction mechanism is used in the present work to study the ignition behaviour of a stoichiometric mixture of methane and air doped with C_3F_7H.

The study of the ignition characteristics of gaseous fuels has been an active area of research for the last 50 years. A major part of these ongoing research activities has been devoted to

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investigate the effects of flame retardants and fire extinguishing agents on the ignition phenomenon. Among these investigations, the work of Babushok et al. *[6]* is quite similar to the present work. These authors numerically studied the effects of a number of fire suppression agents, such as CF_3Br, CF_3H and CF_3I, on the high-temperature reaction of methane with air in a plug flow reactor. They found that the ignition delay time is a function of temperature and flame retardant additive concentration. It was shown that at low additive concentrations, flame retardants actually enhance the combustion reaction and, hence, reduce the ignition delay. Neither the effects of higher additive concentrations (e.g., close to minimum design concentration, MDC) nor other agents, such as C_3F_7H, were addressed.

In the present work, both of these issues are studied by numerical simulation using detailed chemical kinetic modelling techniques. The main objective is to gain some insight into the chemistry involved in the ignition process. This has been motivated by the fact that the ignition phenomenon is closely linked to the initiation and subsequent spread of building fires.

MODEL

In this study, numerical simulations were conducted using the CHEMKIN computer program developed by the Combustion Research Facility of the Sandia National Laboratories [7]. This program is essentially a library of computer codes linked with a chemical species database, which allows the user to perform an efficient kinetic analysis of the gas phase chemical reactions.

The calculations shown here were performed on a stoichiometric mixture of methane, air, and C_3F_7H in a plug flow reactor at initial temperatures between 900-2000 K and atmospheric pressure. Our choices of the mathematical model (plug flow reactor) and test variables, such as fuel type, were primarily dictated hy the ease with which such calculations can be carried out.

The reaction mechanism used in this study was obtained from the literature [3] and consists of three sub-mechanisms: (i) the C_3F_7H mechanism [3], (ii) the GRI-mechanism for CH_4 oxidation [8], and (iii) the NIST (National Institute of Standards and Technology, USA) mechanism for HFCs [9]. The mechanism contains 807 reactions involving 91 species with C, H, N, O and F atoms and incorporates C_1, C_2 and C_3 chemistry.

Two ignition criteria were initially employed. These were (a) the time for a temperature rise of 400 K, and (b) the time for the achievement of the maximum rate of increase in the temperature and rate of decrease in concentration of initial reactants. Preliminary tests showed that the difference between the results produced by both criteria was less than 12%. As a result, for all calculations presented here, the ignition delay time was characterised in terms of the first ignition criteria (400 K temperature rise).

Due to the lack of experimental data for the effects of C_3F_7H on the ignition of gaseous fuel mixtures, the model was validated against the available data [10] for other HFC agents. Our numerical simulations demonstrate good agreement with these data.

RESULTS AND DISCUSSION

The general characteristics (e.g., the temporal history of the temperature rise, fuel and oxygen consumption as well as the production of CO_2) of the combustion reaction occurring during the ignition process of an uninhibited stoichiometric mixture of methane and air **are** shown Figure 1 **As** this figure indicates, the ignition process involves a sudden change in the concentrations of reactant and products, which is also associated with a sharp temperature rise.

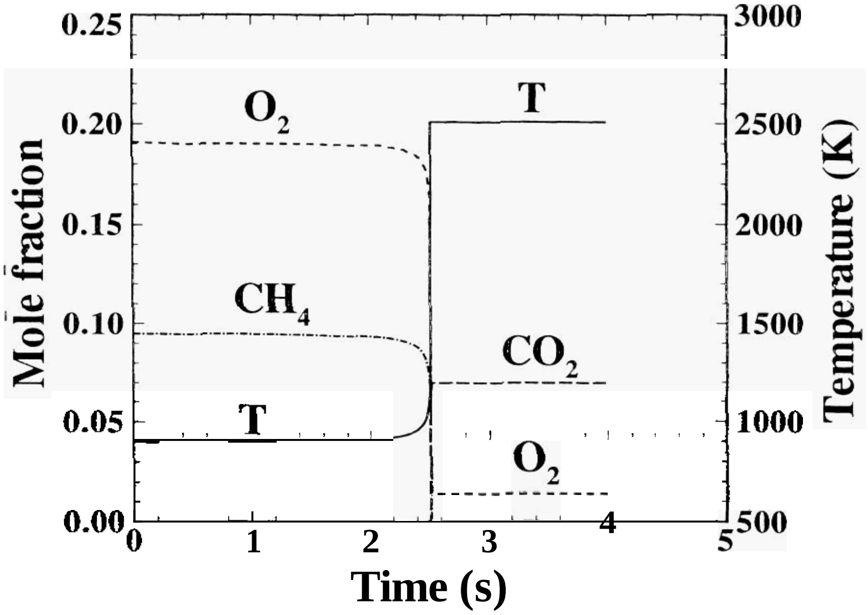

Figure 1. Temperature rise and variation of reactants and products concentrations during ignition of a stoichiometric methane-air mixture at 1 atm and an initial temperature of 900 K.

The variation of the ignition delay time with the initial reactor temperature at various levels of C_3F_7H additive concentration (volume basis) is shown in Figure 2. Two distinct regions can be identified. In the first region ($T \leq 1000$ K) the increase in C_3F_7H additive concentration always results in a subsequent decrease in the ignition delay time and, hence, promotion of the combustion process. Although this agrees with the results reported in literature [10] for other extinguishing agents under similar conditions, it is not consistent with the results of a recent study **[3]** on premixed flames of fuel-lean H_2-air mixtures doped with 1% (mole basis) C_3F_7H.

In the second region ($T > 1000$), however, the trend is reversed. **As a** result, C_3F_7H decreases the ignition delay time and acts as an inhibitor. Since, in reality, the building fires occur under conditions similar to those of the second region, the predictions shown in Figure 2 imply that C_3F_7H has reasonably good inhibition characteristics, especially at concentrations close to its minimum design concentration (7% volume basis).

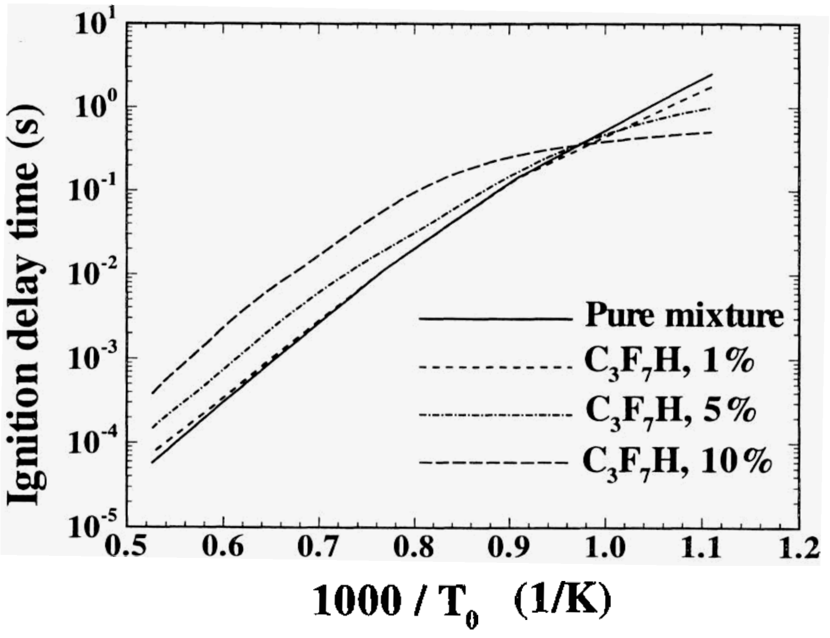

Figure 2. Ignition delay time as a function of initial temperature for a stoichiometric mixture of methane and air at various additive concentrations of C_3F_7H (volume basis).

To investigate the mechanism responsible for the behaviour observed in the first region, the temporal histories of C_3F_7H consumption at 1% and 10% additive concentrations are plotted in Figure 3, at an initial temperature of 900 K. It can be seen that for both cases only a small fraction of the initial concentration of C_3F_7H is consumed prior to ignition. An analysis of reaction pathways at 900 K and 10% additive concentration reveals that the initial C_3F_7H decomposition products play an important role.

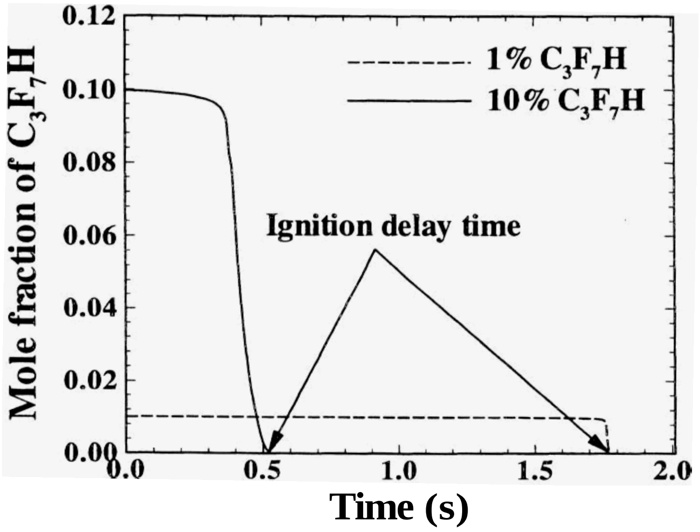

Figure 3. History of C_3F_7H consumption at various additive concentrations for an initial temperature of 900 K.

There are two major routes for initial decomposition of C_3F_7H: (a) uni-molecular decomposition (reaction 1), and (b) molecular elimination of HF (reaction 2). The activation energy of reaction

$$C_3F_7H \rightarrow CF_3 + CF_3\text{-}CHF \tag{1}$$

$$C_3F_7H \rightarrow C_3F_6 + HF \tag{2}$$

(1) is some 84-100 kJ mol-' higher than that of the reaction (2). Even though the elimination reaction has a lower pre-exponential factor (A-factor), at 900 K the rate constant of reaction (1) is likely to be at least three orders of magnitude lower than that of the HF elimination, Thus, under the specified conditions, reaction (2) would be the major initiation reaction. However, under these conditions the rate constant even for reaction (2) is quite small and, hence, hardly any C_3F_7H decomposition occurs prior to ignition (Figure *3)*. **As** a result, C_3F_7H molecules more likely undergo bimolecular reaction with O_2 and act as a source to produce HO_2 radicals. These radicals may attack methane and thereby lead to further propagation of the combustion process.

To check the validity of this hypothesis, the reaction mechanism was modified by not allowing C_3F_7H to react with O_2. The modified mechanism *(Modl)*was then used to repeat the calculation at 900 K and 10%additive concentration. The results were compared with those of the ***Base*** and *Full* cases (Table 1 for the description of each case). As Table 1 shows, the difference between the prediction of the ***Base*** case and that of *Modl* is quite small, indicating that the observed promotion of the combustion process is in fact due to the biomolecular reaction between C_3F_7H and O_2.

Table 1. Comparison of the ignition delay time at 900 K.

Case	Description	t_{ig} (s)
Base	0% additive	1.77
Full	Full reaction mechanism **and** 10%additive concentration	0.52
Modl	Modified reaction mechanism (C_3F_7H is not allowed to react with O_2) and 10%additive concentration	1.90

To study the underlying mechanism responsible for inhibition effects exhibited by C_3F_7H in the second region (T>1000 K) of Figure 2, a chemical kinetic analysis (similar to that performed at 900 K) was performed at 1900 K (Figure 4). This analysis shows that the rate constants of reactions (1) and (2) are closer in value. They both contribute to decomposition of C_3F_7H molecules to produce derivatives like C_3F_7 and C_3F_6. At the same time a significant amount of C_3F_7H is disappeared mainly due to reaction with OH and **O** radicals. Consequently, most of C_3F_7H molecules are consumed prior to ignition, as can be seen in Figure 4. C_3F_7 and C_3F_6 species can further react with OH and **O** radicals and, therefore, interfere with the main chain branching reactions of CH_4 combustion at high temperatures (reactions **3** and 4):

$$H + O_2 \rightarrow OH + O \tag{3}$$

$$O + CH_4 \rightarrow OH + CH_3 \tag{4}$$

Competition between reactions **(3)** and **(4)** and propagation and termination reactions involving C_3F_7 and C_3F_6 and their derivatives results in a slower combustion rate and a lower level **of** heat release. This eventually leads to the inhibition of the combustion process, which is associated with an increase in the ignition delay time (Figure 2).

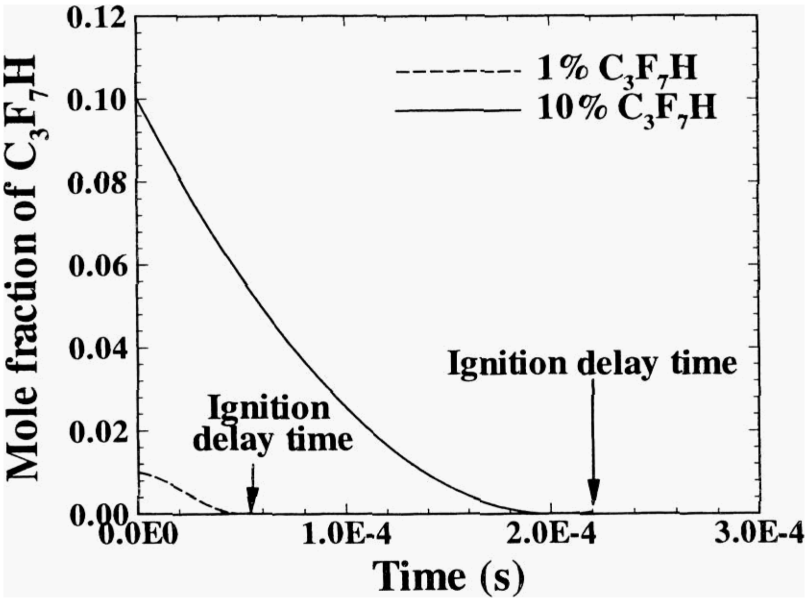

Figure **4.** History of C_3F_7H consumption at various additive concentrations for an initial temperature of 1900 K.

It should be noted that the inhibition capabilities exhibited by C_3F_7H in the second region **are** due to both chemical and physical effects. To isolate these individual inhibition effects, two new cases were modelled and compared with the ***BASE*** and ***Full*** cases at 1900 K. These new cases are (1) ***Mod2*** in which the reaction between **O** and OH radicals and C_3F_7H is not allowed, and (2) ***Phys*** where C_3F_7H is not allowed to react chemically and, hence, has only physical (heat capacity) effects. The results of the comparison are summarised in Table 2.

Table 2. Comparison of the ignition delay time at 1900 K.

Case	Description	t_{ig} (s)
Base	0% additive	**6.0** $\times 10^{-5}$
Full	Full reaction mechanism and 10% additive concentration	2.0×10^{-4}
Pkys	C_3F_7H **is** not allowed to react, 10% additive concentration	1.2×10^{-4}
Mod2	C_3F_7H is not allowed to react with **O** and OH radicals, 10% additive concentration	**1.4** $\times 10^{-4}$

One of the first facts revealed by Table **2** is that the physical effect accounts for about 60% of the total inhibition effect of C_3F_7H. The comparison between the predictions **of *Mod2*** and ***Full*** cases also verifies that the reactions between **O** and OH radicals and C_3F_7H are the major pathways responsible for the observed chemical effect at high temperatures, since the result of ***Mod2*** case is almost the same as ***Phys*** with no chemical effect. However, the small difference between

Mod2 and ***Phys*** cases means there must be some other pathways with chemical effects; although their contributions to the overall chemical effect are much less than those of the pathways identified in this analysis.

CONCLUSIONS

The effects of **a** new halon alternative (C_3F_7H) on the ignition characteristics of a stoichiometric mixture of methane and air were investigated using detailed numerical modelling techniques. It was found that the ignition delay time is primarily a function of initial decomposition products of C_3F_7H. At low temperature, these species promote the combustion of methane by initiating a series of chain reactions. At high temperatures, however, the decomposition products of C_3F_7H inhibit the combustion process. The higher the initial additive concentration, the greater the inhibition effectiveness especially for additive concentration about 5% or more. This has a significant practical implication since such levels of additive concentration are close to the minimum design concentration (7% volume basis) of the actual C_3F_7H fire suppression systems.

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