AN INVESTIGATION OF EXTINGUISHMENT BY THERMAL AGENTS USING DETAILED CHEMICAL MODELING OF OPPOSED-FLOW DIFFUSION FLAMES

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INTRODUCTION

The manufacture of the halons widely used in fire extinguishing systems was banned in 1994 due to their deleterious effect on stratospheric ozone. Since the late 1980s there have been ongoing research efforts to identify replacement agents having comparable properties. This search has proven difficult and continues today with a large directed effort known as the Next Generation Fire Suppression Technology Program (NGP). As part of the NGP, the National Institute of Standards and Technology is investigating whether highly effective thermal agents are feasible. Thermal agents are defined as those that obtain their effectiveness solely by heat extraction and dilution. Excluded from investigation are species that directly or indirectly disrupt the combustion chemistry such as halons, which derive much of their effectiveness by the release of bromine atoms that catalytically remove hydrogen atoms in the flame zone.

A great deal is known about the effects of thermal agents on flames. The paper by Sheinson et al. provides a good introduction [1]. A number of endothermic physical processes can extract heat from a gaseous flame zone, thus lowering the temperature and ultimately leading to flame extinguishment. These include simple heating (i.e., heat capacity) of an agent, phase changes such as vaporization of a liquid or sublimation of a solid, endothermic molecular decomposition (which is classified as a physical process as long as the initial agent and its products do not participate in the combustion chemistry), and simple dilution, which can modify flame temperatures by spreading the heat release over larger volumes and by affecting three-body flame reactions. The flame temperature is also expected to be a function of the thermal diffusivity of an agent.

During the past two decades the understanding of the chemical kinetics involved in combustion has reached the point where realistic detailed mechanisms involving large number of reactants and reactions can be written for simple combustion systems, and mathematical techniques have been developed for simultaneously solving the large number of differential equations that result. While still involving significant approximations, such modeling has advanced to the point where it can be used to gain useful insights into the behavior of practically relevant flames.

This paper describes the results of a detailed chemical kinetic modeling investigation of laminar opposed-flow methane/air diffusion flame designed to provide an improved understanding of the extinguishment of fires by thermal agents. A particular focus was to test the hypothesis that the effectiveness of a thermal agent depends on the location of heat absorption relative to the flame zone. An internal report has been prepared, which summarizes the kinetic modeling in detail and also includes the results of an extensive database search of potential thermal agents and modeling results for the effectiveness of thermal agents in cooling liquid surfaces [2].

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DETAILED CHEMICAL KINETIC MODELING

A number of different types of combustion systems have been modeled using detailed chemical kinetic approaches including plug flow reactors, perfectly stirred reactors, premixed laminar flames, and opposed flow laminar diffusion flames. For studies of fire extinguishment, we have chosen an opposed flow laminar diffusion flame model because for the majority of fires the fuel and air are initially separated and therefore burn as diffusion flames. Most fires are large enough to be turbulent, so a laminar flame model is not strictly correct. However, the most widely used model for turbulent combustion incorporating detailed chemistry is the laminar flamelet concept, which treats the combustion as laminar flame sheets subject to the local strain rate field associated with the fire-induced motions of the fluid [3,4]. Thus, the opposed flow diffusion flame is a particularly appropriate detailed chemical kinetic model for describing fire behavior.

Three configurations of opposed flow diffusion flames have been described in the literature: opposed jet, flow over a porous cylinder, and flow over a porous sphere. For the porous bodies, fuel typically flows from the surface, and the surrounding flow is the oxidizer. The three configurations are related in that a diffusion flame is stabilized in the region near the stagnation point in the flow. Numerous papers in the literature discuss these types of flames. Two excellent reviews have been provided by Tsuji [5] and Dixon-Lewis [6]. The review by Tsuji includes a discussion of the use of such burners to characterize flame inhibition experimentally. Recently, an opposed jet experiment has been used to investigate potential replacement agents for halons [7]. The most common of the three configurations used in the recent past is the opposed jet laminar diffusion flame, which was chosen for the current investigation.

Laminar opposed flow diffusion flames are usually modeled as one-dimensional flow systems by using a similarity transform to reduce the two-dimensional equations. Fuel and oxidizer velocity profiles at the burner exits are most often assumed to be those appropriate either for potential flow, which has a constant strain rate (a_p) (velocity gradient), or for exit plug flow, which has a local strain rate (a) equal to 0 s^{-1}. Since the latter boundary condition corresponds more closely to most experiments, it is used for the calculations reported here. As the opposed flow velocities are increased, the flame is subjected to higher and higher strain rates. It is well known that, as the strain rate becomes larger, the flame gradually becomes weaker and weaker until it abruptly undergoes extinction [8,9]. A number of different parameters are used to quantify the effect of strain rate on a laminar flame including the constant strain rate (a_p); a global strain rate (a_g); the maximum strain rate outside of the thermal boundary layer on the oxidizer side (a_o); and the stoichiometric scalar dissipation (Π_s).

For this investigation, a series of laminar opposed flow diffusion flames of methane and oxidizer has been calculated as a function of their opposed flow velocities (assumed to have equal magnitudes) and the concentration of various thermal agents added to the air. For each concentration of added agent, an extinction condition is identified that corresponds to a given velocity magnitude and corresponding measures of strain rate and stoichiometric scalar dissipation. A focus of this work is to identify the minimum concentration of an agent required to extinguish buoyancy dominated fires. The cup burner is an example of one experimental approach for determining this concentration. The extinguishing concentration is therefore expected to correspond to a particular extinction condition.

CALCULATIONAL APPROACH

The goal is to calculate the effects of thermal agents on laminar methane/air opposed flow diffusion flames. There are a number of codes described in the literature for making such calculations. The code Oppdif [10] developed by Sandia National Laboratories was chosen. This code is now available commercially from Reaction Design* of San Diego, CA. Oppdif is built on a number of general purpose subroutines, collectively known as Chemkin-III [11], which handle many of the tasks associated with the calculation. Data describing the reaction mechanism and thermodynamic and transport properties are either incorporated in Oppdif or accessed as databases.

Oppdif solves the psuedo-one-dimensional equations describing a laminar axisymmetric opposed flow diffusion flame. The approach is that originally used by Kee et al. [12] for premixed flames to solve problems in which the radial velocity gradient is constant at the boundaries and later extended to diffusion flames by Chelliah et al. [13] This condition includes plug flows with $a = 0\ s^{-1}$ at the burner exits, which were used for all of the calculations here.

A detailed chemical kinetic mechanism is required to model the flame. After reviewing the literature, we chose the widely used methane/air mechanism developed with the support of the Gas Research Institute. The version used was GRI-Mech 1.2 [14] which consists of 32 chemical species undergoing 177 reactions. One- and two-carbon reactions are included. Thermodynamic and transport data are provided as separate files. The mechanism was created by the GRI-sponsored researchers by starting with appropriate estimates for the rate constants and then optimizing the mechanism to provide the best agreement with experimental measurements in such systems as premixed flames, shock tube studies, and flow reactor investigations [14]. It should be noted that the mechanism was not optimized using diffusion flame results.

To determine the extinction behavior for a flame as functions of flow conditions and agent concentration, a burning solution was first obtained for a particular combination of methane and oxidizer having relatively low fuel and oxidizer exit velocity magnitudes. The velocity magnitudes were then increased until a condition was reached where the flame went out or a solution was not obtained. By approaching the extinction velocity in small increments, it was possible to obtain the extinction point to within a step size of 0.01 cm/sec.

Figure 1 shows a plot of maximum temperature, T_{max}, versus flow velocity (equal magnitudes for the fuel and oxidizer opposed velocities) calculated for a laminar opposed flow methane/air diffusion flame.

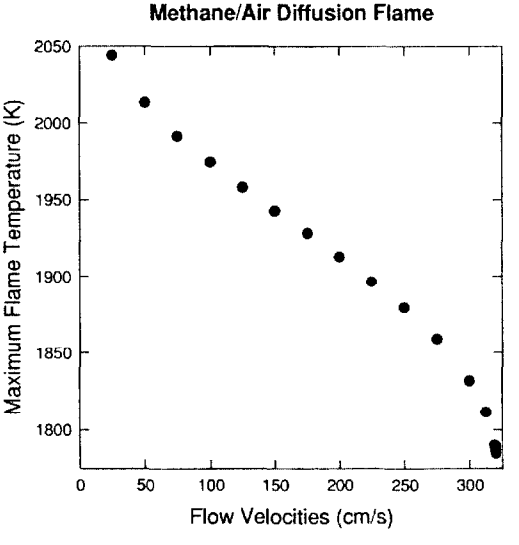

Figure 1. Maximum flame temperature versus exit velocity magnitudes.

*Certain commercial equipment, instruments, or material are identified herein to specify the experimental procedure adequately. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

The fuel is 100% methane and air is assumed to be composed of 88.1% N_2, 21.0% O_2, and 0.9% Ar by volume. As expected, T_{max} decreases with increasing velocity. Extinction is calculated to occur for a velocity of 320.12 cm/sec with a maximum flame temperature of 1785 K [8,9].

The maximum strain rate on the oxidizer side for the extinction condition is $*a_o* = 509$ sec^{-1}. This value is roughly 25% higher than measured experimentally [7,13,15]. Tanoff et al. have shown that calculated values of a_o are highly dependent on the detailed mechanism used [16]. In their work, GRI-Mech also overpredicts the extinction strain rate.

METHANE FLAMES BURNING IN AIR DILUTED WITH THERMAL AGENTS

Despite the large number of studies previously reported for methane combustion, we were only able to identify two experimental measurements of extinguishing concentration for methane flames burning in air diluted with an added thermal agent. Both studied the effect of added nitrogen. Simmons and Wolfhard [17] and Ishizuka and Tsuji [18] reported extinguishing concentrations of 33.8% and 31.9%, respectively. These two measurements are in good agreement. Simple averaging yields an estimate of 33% added nitrogen. Simmons and Wolfhard calculated the adiabatic flame temperature for a stoichiometric premixed flame corresponding to their extinction condition as 1820 K. Ishizuka and Tsuji used thermocouples to measure the maximum flame temperature in their diffusion flame as 1483 K for the extinguishing condition. A series of calculations was performed for methane opposed-flow diffusion flames reacting with air containing various percentages of added nitrogen. Figure 2 shows the results. Several points are immediately obvious. As the percentage of added nitrogen increases, the fuel and oxidizer exit velocity magnitudes sufficient to cause flame extinction decrease. The maximum flame temperature at extinction also decreases as the nitrogen concentration increases. The plots of T_{max} versus velocity magnitude become more steep as the concentration of nitrogen increases.

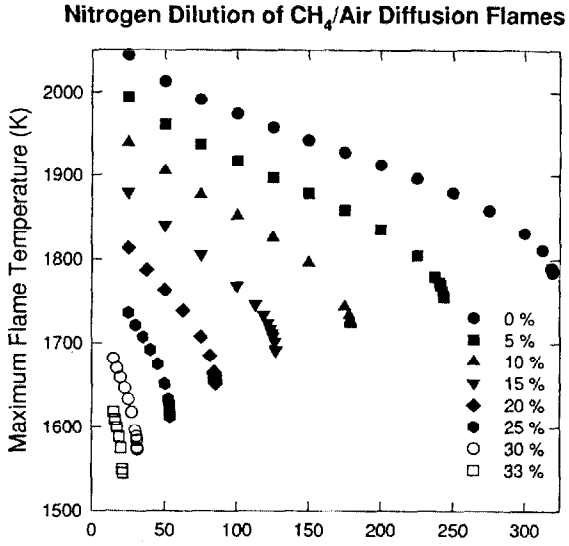

Figure 2. Maximum flame temperature versus flow velocity magnitudes for methane burning in nitrogen-diluted air.

The experimental concentration of added nitrogen that extinguishes the flame is 33%. The calculated value of T_{max} at extinction for this concentration is 1545 K. This is very close to the experimental value of 1483 K [18]. In fact, the agreement is probably better than indicated since the thermocouple measurements of Ishizuka and Tsuji were not corrected for radiative heat losses, which would be expected to decrease the measured temperature. The calculated temperature is expected to be a slight overestimate due to neglect of the radiation heat losses.

These estimates for the maximum flame temperature at extinguishment are consistent with others available in the literature. Sheinson et al. indicate that hydrocarbon combustion is not sustainable when the maximum flame temperature drops below roughly 1600 K [1]. This estimate is

based upon work by Roberts and Quince [19]. Very recently, Babb et al. have reported radiation-corrected thermocouple temperature measurements in heptane flames near their extinction points using air diluted by N_2 and CO_2 [20]. For both thermal agents, the maximum flame temperatures at extinguishment were on the order of 1500 K. Similar measurements using propane as fuel gave maximum flame temperatures of 1600 K and 1700 K for added N_2 and CO_2, respectively.

For the conditions corresponding to extinguishment with added nitrogen, the velocities of the fuel and air at extinction are calculated to be 21.42 cm/sec. Corresponding values for the various measures used to characterize the flow condition at extinction are $a_g = 37.5\ \text{sec}^{-1}$, $*a_o* = 27.0\ \text{sec}^{-1}$, and $\Pi_s = 0.80\ \text{sec}^{-1}$.

An important question concerning the extinction of diffusion flames is—What strain rate is appropriate to use when determining the minimum value of an added thermal agent required to extinguish diffusion flames at normal gravity? The only discussion of this point of which we are aware was presented by Hamins et al. [21]. These authors compared cup-burner measurements (heptane fuel) of extinguishing concentrations for a variety of agents with corresponding measurements made in a counterflow flame. The counterflow measurements were made over a range of flow velocities, which were characterized in terms of a global strain rate appropriate for an air flow impinging on a liquid surface. In agreement with the current calculations, the required strain rate to cause extinction of the counterflow flame decreased with the concentration of added agent. When the concentrations of added agents for the opposed flame were comparable to those observed in the cup-burner test, the global strain rate was on the order of 50 sec^{-1}. Due to use of different boundary conditions and fuels between the current investigation and those for Hamins et al. [21], as well as slightly different definitions for the global strain rates, absolute quantitative comparisons are not appropriate. However, it is clear that the strain rates have comparable magnitudes in each case. It is important to note that the strain rate appropriate for characterizing the extinguishing condition is much lower than typically used for experimental and modeling investigations of opposed-flow laminar diffusion flames.

It is interesting to speculate about why lower and lower strain rates can not be sustained for flames at normal gravity. The most likely reason is that buoyancy effects result in a lower limit for the minimum strain rate perpendicular to a flame surface. Buoyancy always accelerates hot combustion gases relative to the cold oxidizer with the result that the flame surface is subject to a nonzero strain rate. The results of Hamins et al. [21] and the current findings suggest this minimum strain rate is on the order of a few tens of inverse seconds.

As already pointed out, we have identified no additional measurements of extinguishing concentrations for thermal agents added to methane/air diffusion flames. However, Ishizuka and Tsuji did make measurements for methane burning in an artificial "air" consisting of 21% oxygen and 79% argon [18]. This "air" was diluted with argon until extinguishment occurred. The result corresponded to an added argon concentration of 54.3%. The measured maximum flame temperature at extinguishment was 1443 K, or roughly 40 K less than for standard air diluted with nitrogen. To test the ability to predict extinguishing concentrations of added thermal agents, a series of calculations for argon "air" diluted with argon were made.

Figure 3 shows a plot of the maximum calculated flame temperature as a function of the percentage of argon added to the argon "air" and the fuel and oxidizer velocity magnitudes. Comparison with Figure shows that replacing nitrogen with argon has a dramatic effect on the flame behavior. First, flame temperatures are considerably higher for a given diluent concentration and fuel and oxidizer velocity magnitudes for the argon "air." This is due to the lower heat capacity of argon as compared to nitrogen. As a result of the increase in temperature, much higher flow velocities are required to generate the strain rate necessary to cause extinction. For the same reason, higher concentrations of argon must be added to achieve extinguishment than in the nitrogen case.

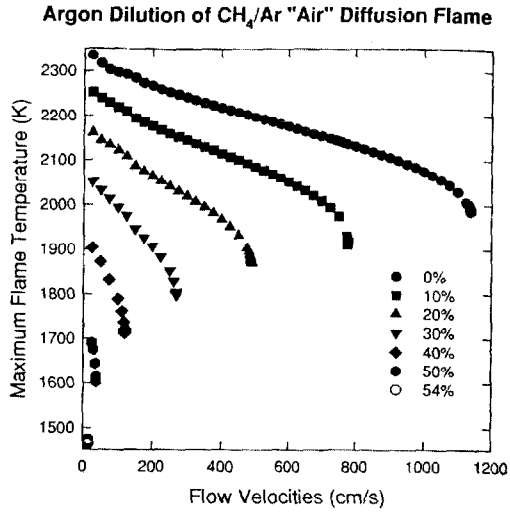

Figure 3. Maximum flame temperature versus exit velocity magnitude for methane flame in Ar "air."

The flame formed by an oxidizer having 50% argon is calculated to undergo extinction with a maximum temperature of 1610 K and methane and oxidizer velocity magnitudes of 37.8 cm/sec. The corresponding results for 54% argon, corresponding to the experimental extinguishment value, are 1473 K and 15.9 cm/sec. These values are both slightly smaller than found for the methane/air flame diluted with nitrogen, 1545 K and 21.4 cm/sec, respectively. However, they are remarkably close when one recalls that the use of argon instead of nitrogen should result in a significantly different flame structure due to differences in heat capacity and thermal diffusivity between nitrogen and argon. In fact, if one simply assumes that extinguishment occurs for the same maximum flame temperature, i.e., roughly 1550 K, as for the nitrogen-diluted air flame, it is possible to estimate the required argon concentration as 52% (Figure 3). This is only 4% less than the experimental value. Thus, an assumption that flame extinguishment occurs for the concentration necessary to reduce the maximum calculated flame temperature at extinction to 1550 K should provide an excellent estimate for the percentage of an arbitrary thermal agent required to extinguish a fire. This approach is used for estimating extinguishing concentrations in the present work.

Opposed flow diffusion flame calculations have been used to estimate the required extinguishing concentrations, i.e., the concentration necessary to lower the maximum flame temperature at extinction to 1550 K, for methane burning in air diluted with Ar, He, CO_2, and H_2O. Each of these gases is expected to act primarily as a thermal agent. The resulting plots (not shown) of maximum flame temperature versus the magnitudes of the fuel and oxidizer velocities exhibit trends similar to those for nitrogen and argon shown in Figures 2 and 3, respectively. The estimates for extinguishing concentration are tabulated below (Table 1).

As already discussed, the only experimental values for opposed flow methane diffusion flames we have identified are for nitrogen dilution. Cup-burner determinations of extinguishing concentrations using heptane as fuel have been reported for some of these agents by Sheinson et al. [1], Babb et al. [20], Hamins et al. [22], and Moore et al. [23]. These values are included in Table 1. The maximum difference between values calculated for methane and the experimental values for

TABLE 1. EXTINGUISHING CONCENTRATIONS (MOLE FRACTION) OF THERMAL AGENTS.

Thermal Agent	Current Work	Cup Burner [1]	Cup Burner [20]	Cup Burner [22]	Cup Burner [23]
Nitrogen	0.33	0.30	0.33	0.32	0.30
Argon	0.43	0.41	——	0.41	0.38
Helium	0.34	0.32	——	0.31	——
Carbon Dioxide	0.22	0.21	0.20	0.23	0.20
Water	0.28	——	——	——	——

heptane is 12%, with the vast majority being less than 10%. With the exception of carbon dioxide, the cup-burner measurements are somewhat lower than for the counterflow flame. These differences could be due to the use of different fuels or to the effects of burner configuration. The heptane fires are burning just above a liquid fuel in a coflow of oxidizer, and it may be easier to blow out this type of flame than the opposed flow diffusion flame, which is stabilized away from surfaces. The close tracking of the calculated results and the experimental findings suggest that detailed chemical kinetic modeling can accurately predict the amount of a thermal agent required to extinguish opposed-flow diffusion and cup-burner flames.

The differences in the extinguishing concentrations of helium and argon are interesting since these agents are both monatomic gases and have the same heat capacities. The difference is clear in both the calculations and the experimental values. The fact that helium is a more efficient extinguishing agent means that at least one other parameter, in addition to heat capacity, is important in determining extinguishing efficiency. A related observation was reported by Coward and Hartwell for the inerting of premixed flames and was attributed to the much higher thermal conductivity of helium, which distributes the heat of combustion over a larger region of space and therefore weakens the flame [24]. The same explanation is most likely valid for diffusion flames. Sheinson et al. reached the same conclusion [1].

Comparison of the dependence of calculated maximum flame temperature on the fuel and oxidizer exit velocity magnitudes for the different thermal agents shows that, for given velocities and extinction temperatures, they have very similar shapes. This is true despite the fact that the amount of added agent and, therefore, the oxygen concentration and stoichiometric ratio vary dramatically with agent. This is confirmed in Figure 4, which shows the maximum flame temperature at extinction as a function of fuel and oxidizer exit velocity magnitudes for the five thermal agents added to air as well as the results for argon added to argon "air." The data fall within a narrow band on either side of a well-defined curve.

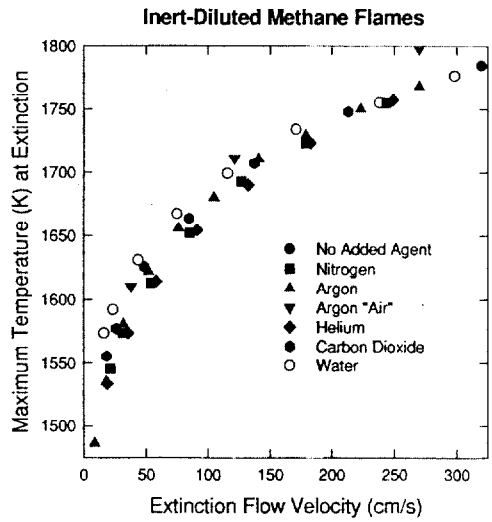

Figure 4. Maximum flame temperature versus exit flow velocity magnitude for thermal agents.

A survey of thermodynamic data bases has identified potential halon replacements based on their ability to absorb heat [2]. One example is methoxy-nonafluorobutane ($C_4F_9OCH_3$; HFE7100), which is available commercially [25]. The required extinguishing concentration was estimated as 5.5% assuming an extinction temperature of 1550 K. Two experimental measurements of the concentration of HFE7100 required to extinguish diffusion flames have been identified. Unpublished measurements from the New Mexico Engineering Research Institute using a standard cup burner with heptane fuel yielded a value of 6.1 vol.%.* In a patent disclosure, Flynn and Scott also reported that 6.1% was sufficient to extinguish a butane flame in a "micro-cup burner" [26]. These values are 11% higher than estimates from detailed chemical kinetic modeling.

SURROGATE AGENT STUDIES OF EXTINCTION AND EXTINGUISHMENT

An important advantage of modeling investigations is the ability to perform calculations for conditions that are not physically possible in order to learn details concerning the role of various parameters. One question, which has been the subject of speculation, is the relative importance of heat extraction and dilution on the effectiveness of a thermal agent. Here dilution refers to any effects of a thermal agent not simply due its ability to extract heat. To obtain insights into this behavior, an artificial agent was created by starting with argon and setting its heat capacity to zero. Direct comparison with the results for added argon allows the relative roles of heat extraction and dilution to be characterized. Sheinson et al. have discussed the effects of dilution on extinguishment [1]. They concluded that they are relatively small compared to direct heat removal due to heat capacity for the thermal agents CF_4 and SF_6.

Figure 5 is a plot of calculated maximum flame temperature versus fuel and oxidizer velocity magnitudes for the zero-heat-capacity argon added to air. It is obvious that this species does decrease the strength of the flame, but its effect is much smaller than for the argon. Based on an extinguishment temperature of 1550 K, the extinguishing concentration can be estimated as 73% or roughly 1.7 times of the amount required for argon. This corresponds to an oxygen concentration of 5.7%. Interestingly, the dependence of the maximum flame temperature at extinction on the fuel and oxidizer velocities is very similar for both sets of calculations. Assuming that the effects of heating an inert and dilution are additive and linear in concentration, the effectiveness of Ar as a thermal agent is estimated to be 59% due to dilution and 41% due to heat extraction. Comparison of the detailed flame structures for methane flames in air and in air diluted with zero-heat-capacity argon shows that the primary reason for the weakening of the flame burning in the diluted

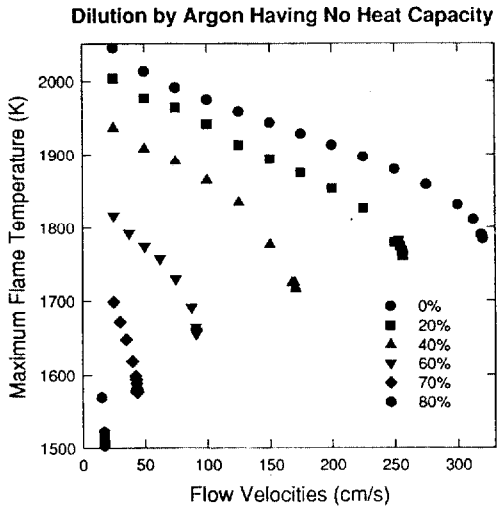

Figure 5. Maximum flame temperature versus exit velocity magnitude for agent with no heat capacity.

* Tapscott, R. E., Personal Communication, 26 February 1999.

air is the passage of more oxygen through the flame to the fuel side. The unreacted oxygen that leaks through the flame front acts as a thermal agent.

One of the goals of the current work was to test the hypothesis that the effectiveness of a thermal agent depends on the location, relative to the high temperature flame zone, where heat extraction occurs. A surrogate thermal agent, X, was used for these calculations. The molecular weight, thermodynamic properties, and transport properties of X are identical to those of argon, but it can undergo a simple reaction with ambient gases to generate a new species, Y, that is,

$$X + M \rightarrow Y + M \tag{1}$$

Y is also very similar to argon, the only difference being that its heat of formation is assigned an arbitrary positive value instead of being zero. As a result, when Reaction (1) takes place it extracts heat and cools the local surroundings by an amount equal to the heat of reaction, ΔH_{X-Y}. Since X and Y do not react with any other species, the reaction is simply a heat sink and, therefore, meets the definition of a thermal agent.

The rate constant for Reaction (1) is expressed as

$$k_{X \rightarrow Y} = A T^{\beta} e^{-E_a / RT} \tag{2}$$

where A is the pre-exponential factor, β is the temperature exponent, E_a, is the energy of activation, R is the gas constant, and T is temperature. By varying the parameters A, β, and E_a, it is possible to change the rate and temperature range over which the reaction occurs and hence the location relative to the flame zone for heat extraction. For the following calculations, initial values were chosen for A and β, and only the value of E_a was changed in order to vary k_{X-Y}.

Figure 6 compares calculated flame temperature versus distance from the fuel exit for two flames having fuel and oxidizer exit velocity magnitudes of 25 cm/sec and with 5% X added to the air. For each, $A = 1 \times 10^{10}$ cm^3/(mole-s), $\beta = 0$, and $\Delta H_{X-Y} = 96.1$ kJ/mole. The only difference between the two calculations is the value of E_a, which equals 25.1 kJ/mole, for one and 50.2 kJ/mole for the other. For the lower E_a, X begins to react immediately upon leaving the oxidizer exit, which results in the temperature drop evident on the oxidizer side for positions well removed from the flame zone. When the E_a is increased to 50.2 kJ/mole, the conversion of X to Y is very slow at room temperature, and there is no significant drop in temperature in the ambient region of the flow. However, as the temperature increases, X begins to convert to Y, and heat is absorbed in higher temperature flame regions. Interestingly, maximum flame temperatures are identical within the uncertainty of the calculations. Since flame extinguishment depends primarily on the maximum flame temperature at extinction, this suggests the effectiveness of a

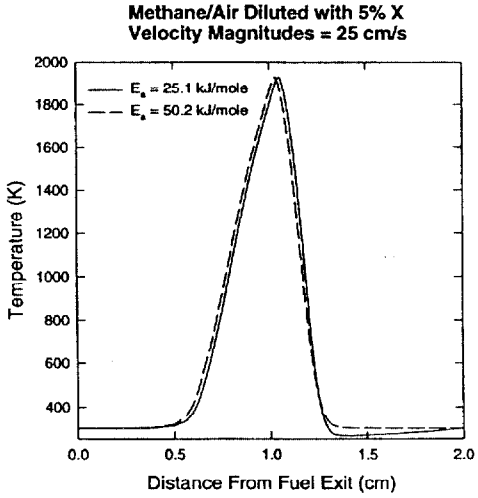

Figure 6. Temperature versus distance from fuel exit for methane/air diluted with 5% X flame.

thermal agent is independent of the spatial location where the heat extraction occurs, indicating that the original hypothesis concerning the effect of heat extraction position was incorrect.

A complete set of calculations was carried out for X having $\Delta H_{X-Y} = 96.1$ kJ/mole and E_a = 41.8 kJ/mole. Based on an extinction temperature of 1550 K, the extinguishing concentration for X is estimated to be 15.9%. The corresponding value for argon was 43%. Thus, the heat extracted by the reaction of X to Y has reduced the amount of agent required by nearly 2/3. Figure 7 compares calculated values of maximum flame temperature as a function of velocity magnitude for 15%, 30%, and 45% added argon with the corresponding results for 5%, 10%, and 15% X. The two sets of data fall close together, but agreement is not complete. At the lower concentrations the results for X fall slightly below those for Ar, while the opposite is true for the highest concentrations.

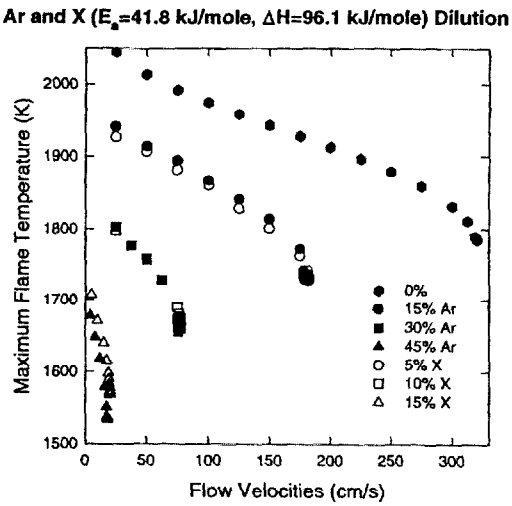

Figure 7. Maximum flame temperature is plotted versus exit velocity magnitude for methane flames in air diluted with Ar and X having $E_a = 41.8$ kJ/mole.

The effect of doubling the heat absorbed by X was considered by running a series of calculations for $\Delta H_{X-Y} = 192.1$ kJ/mole. From these results the extinguishment concentration for X with the higher heat absorption can be estimated as 9.7%. This value is roughly 60% of that found with $\Delta H_{X-Y} = 95.2$ kJ/mole, or 20% higher than would be expected if flame extinguishment was due solely to the heat extracted. The most likely source for this differences, as well as that seen in Figure 7, is the effect of dilution discussed earlier. The concentration of added agent required for flame extinguishment decreases as the amount of heat it can absorb increases, but the decreased concentration reduces the effectiveness of dilution, with the result that the effectiveness of extracting additional heat is offset somewhat.

The role of dilution has implications with regard to estimates of extinguishing efficiency for thermal agents, which are often obtained by taking ratios of heat capacities for various agents. If the agents have a large heat capacity difference, and the percentages required for extinguishment therefore differ substantially, a simple linear dependence on heat capacity should not be observed. In fact, the agent having the largest heat capacity should be less effective than expected, as observed in the current calculations.

SUMMARY

It has been shown that detailed chemical kinetic modeling can be used to make quantitative predictions of the amount of a thermal agent required to extinguish a fire. Results for four well-known thermal agents are in good agreement with experimental values. The calculations suggest that strain rates in fires are on the order of a few tens of inverse seconds and that the maximum flame temperature at extinction for the extinguishing condition is approximately 1550 K. The use of surrogate agents has revealed that (1) dilution effects are due to an increase in the amount

of O_2 bleeding through the flame front and (2) the role of dilution is relatively small as compared to heat absorption. The location of the heat absorption relative to the flame front does not affect the ability of a thermal agent to extinguish a flame as long as the agent is convected to the flame zone. While good qualitative estimates of flame extinguishing effectiveness can be obtained based solely on the ability of an agent to absorb heat, the estimates are not perfect due to dilution effects.

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