NUMERICAL INVESTIGATION OF THE SENSITIVITY OF PREMIXED FLAMES TO LOCALIZED CHEMICAL INHIBITION

Marc D. Rumminger*, Valeri Babushok, Gregory T. Linteris
National Institute of Standards and Technology, Gaithersburg MD 20899, USA

(marc.rumminger@nist.gov, vbabushok@nist.gov, linteris@nist.gov)

A presentation at the 1998 Spring Meeting of the
Western States Section of the Combustion Institute, Berkeley, CA

A brute force sensitivity technique that involves perturbation of reaction rate in a region that can be defined by temperature, species concentration, time or space is presented. The technique is used to investigate the sensitivity of premixed methane-air flames to several different chemical perturbations: reduction of the $H+O_2 \leftrightarrow OH+O$ reaction rate, reduction of the $CO+OH \leftrightarrow CO_2+H$ reaction rate, catalytic scavenging of radicals by a perfect inhibitor and inhibition by CF_3Br (halon 1301). The results indicate that the flame speed of a premixed methane-air flame is reduced most when the perturbation is near the regions of maximum radical mole fraction and maximum reaction rates. Calculations of CF_3Br-inhibited flames find a temperature of maximum influence that is higher than previous suggestions for Br-based inhibitors. Each of the perturbations have a negligible effect below 1200 K. The effect of equivalence ratio is investigated. For $H+O_2$ perturbation and addition of the perfect inhibitor, location of the perturbation that results in minimum flame speed for lean (ϕ=0.7), rich (ϕ=1.3), and stoichiometric (ϕ=1.0) flames follows the relative position of the peak H-atom mole fraction. The calculations with the perfect inhibitor show that inhibition in just a portion of the flame can cause a significant reduction in flame speed. Sudden activation and deactivation of the perfect inhibitor are simulated in a stoichiometric flame. In both cases, the effect of the inhibitor is small when the activation or deactivation temperature is below 1700 K.

INTRODUCTION

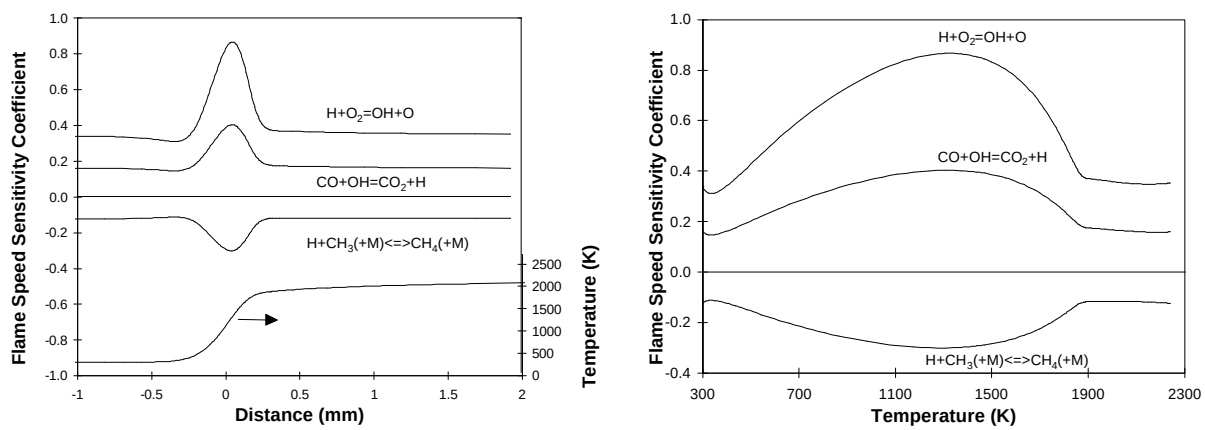
For purposes of analysis or discussion, researchers divide a premixed flame into zones, with the number of zones and their descriptions varying. For example, to facilitate an activation-energy asymptotics calculation, Williams [1] divides the flame into a "convective-diffusive zone" and a "reactive-diffusive zone." In a discussion of premixed flame structure, Westbrook and Dryer [2] divide a premixed flame into five zones to describe the chemical and physical processes in the flame. Understanding the effect of reactions proceeding in different zones of a premixed flame can provide insight into flame structure, pollutant formation, flame inhibition and other phenomena. For example, determining which zone of a flame is most sensitive to chemical or thermal inhibition can provide information to assist the search for new fire suppressants.

---

* National Research Council / NIST postdoctoral fellow

In this paper we present a brute-force sensitivity technique that can be used to investigate the sensitivity of a flame to reactions proceeding in different zones. Brute-force sensitivity techniques involve repeated calculations with one parameter varied while the others are held constant [3-5]. Although such calculations have the disadvantage of high computational cost, they can still be affordable for one-dimensional laminar flames. More computationally efficient techniques of sensitivity analysis exist [6-7] (sometimes called the "direct method," "local method," or "differential method"), but their results can be hard to interpret, and they have limited versatility and applicability [8].

The calculation of burning rate sensitivity using the direct method is not straight-forward. For a one-dimensional premixed flame, a sensitivity calculation results in a flame speed sensitivity coefficient for each reaction at each grid point [6]. Because the flame speed is a global (i.e., not spatial) parameter, the maximum sensitivity coefficient is typically used for interpretation of results. Figure 1 shows the sensitivity of burning rate to several reactions for a freely-propagating, premixed, stoichiometric methane-air flame (details are given below in the "Flame Modeling Approach" section). In Figure 1a, the x-axis is distance, while in Figure 1b the x-axis is temperature. The self-similarity of the curves [6] leads to each sensitivity coefficient having the same relative spatial (and thermal) characteristics. It is questionable to conclude from Figure 1b that the flame speed is most sensitive to changes in reaction rate at 1500 K; some reactions are clearly only important below this temperature, while others are important above.



a) b)

Figure 1: Sensitivity coefficients for flame speed in a one-dimensional stoichiometric methane-air flame, a) distance as the independent variable with the location of zero corresponding to the point of 50% CH_4 consumption, b) temperature as the independent variable.

Our sensitivity technique ("band sensitivity") can be used to obtain quantitative information about the sensitivity of a flame to a localized perturbation. Reaction rates of selected chemical reactions are perturbed in a region that can be defined by temperature, species concentration, time or space. For example, by varying the region

in which inhibition occurs, we can simulate an inhibitor that is effective in a certain temperature range, such as inhibiting molecules formed from a precursor but stable only below a certain temperature. Such simulations can help guide the search for new fire suppressants by allowing researchers to ask "what if?" questions about new compounds, even with limited information about the kinetics.

In this paper, we use the band sensitivity technique to investigate flame inhibition, with inhibitor concentrations less than those typically used to suppress fires. Although we do not directly address fire suppression, the magnitude of the burning velocity reduction used here is adequate for demonstrating the technique and gaining insight into flame behavior under these conditions. To this end, we use the technique to examine numerically the sensitivity of premixed flames to several types of perturbation. The change in laminar flame speed is used as a measure of the sensitivity of the overall reaction rate to the perturbation. We numerically investigate which region of a one-dimensional premixed CH_4/air flame is most sensitive to four types of perturbation: reduction of chain branching, reduction of the heat release rate through CO oxidation, radical scavenging by a perfect flame inhibitor [9], and inhibition by CF_3Br (halon 1301). We use a variation of the technique to simulate rapid activation and deactivation of a perfect flame inhibitor.

NUMERICAL TECHNIQUE

Band Sensitivity Technique

A reacting system is perturbed by modifying selected reaction rates in a region or regions (also called "bands"). The band can be defined by temperature, time, space or species concentration. The perturbation can affect a single reaction (for example, $H+O_2 \leftrightarrow OH+O$), a class of reactions (for example, CO_2 formation reactions), or a portion of a chemical mechanism (for example, reactions involving Br-containing species in a mechanism for CF_3Br inhibition).

For bands defined by temperature, a perturbation factor B_i is defined for the selected group of reactions as

$$\begin{array}{ll} B_i = 1 & T < T_b \\ 0 < B_i < 1 & T_b \text{ £ } T \text{ £ } T_b + \Delta \\ B_i = 1 & T > T_b + \Delta \end{array}$$

where T is the gas temperature, T_b is the temperature at the low edge of the band, and Δ is the size of the band. Figure 2-a illustrates the band shape for this example. The reaction rates of the selected reactions are multiplied by B_i and the rest of the reactions are not directly disturbed (i.e. B_i=1). To study different types of perturbation, the band depth (the magnitude of B_i), width (D), and shape (the variation of B_i with T) can be varied. For study of flame inhibition, the pertinent reactions are turned *off* outside the band (B_i=0) and turned *on* inside the band (B_i=1), as illustrated in Figure 2-b. For modeling of activation or deactivation of an inhibitor a forward-facing or backward-facing step function is used; here, the inhibition reactions are turned off (or on) below a

certain temperature and turned on (or off) above that temperature, as shown in Figure 2-c and d.

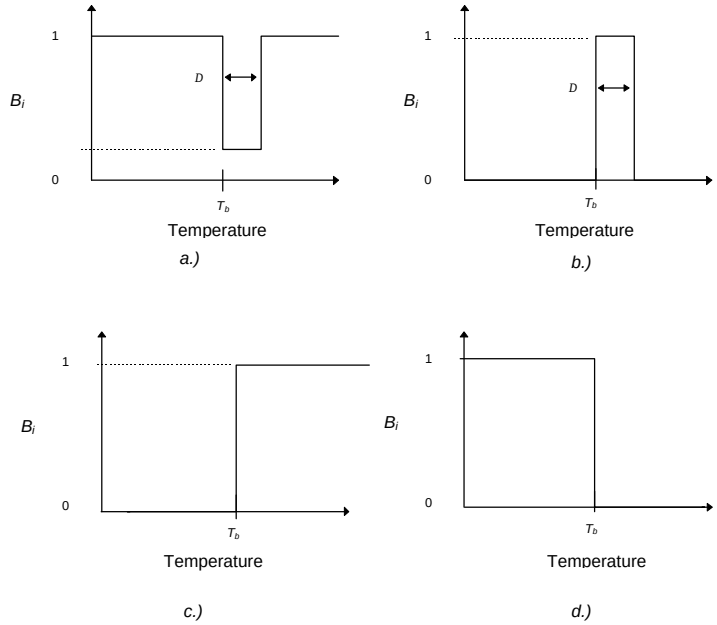


Figure 2: Shapes of the reaction rate variable. a) profile used for perturbation of chain branching and heat release, b) profile used for perfect inhibitor and CF_3Br , c) profile that approximates rapid inhibitor activation, d) profile that approximates rapid inhibitor deactivation.

In practice, the band is smoothed at the edges to avoid numerical convergence problems caused by infinite gradients. For the computations described here, the smoothing function is $B_i = a - b \operatorname{erf}(-c\, T^* + d)$, where $T^* = (T - T_b) / \Delta$ at the low temperature edge and $T^* = (T_b + \Delta - T) / \Delta$ at the high temperature edge. The constants *a*, *b*, *c*, and *d* are selected such that the width of the smoothed portion of the band is approximately $0.1 \cdot \Delta$ at each end.

Flame Modeling Approach

The Sandia *Premix*†[10] flame code is used with the kinetic [11] and transport [12] subroutines to simulate the freely-propagating premixed flame, with the *Chemkin* subroutine CKRAT modified to accommodate the band sensitivity procedure. Part of the post-processing is performed using a graphical postprocessor [13]. For all calculations the initial reactant temperature is 300 K and the pressure is 1 atm. For numerical convergence, an absolute tolerance of 10^{-10} is used, and a relative tolerance of 10^{-6} is used. The "GRAD" parameter is set to 0.15, and "CURV" is set to 0.35 for all of the calculations except those involving CF_3Br, where the higher values of GRAD (0.35) and CURV (0.55) are used to reduce the calculation time.

† Certain commercial equipment, instruments, or materials are identified in this paper to adequately specify the procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for the intended use.

The kinetic and thermodynamic data of GRI-Mech 1.2 [14] (32 species and 177 chemical reactions) serve as a basis for describing the methane combustion, except when the inhibitor is CF_3Br. In that case, the mechanism of Babushok et al. [15] describes the C_1/C_2 hydrocarbon chemistry and the halogen chemistry (70 species and 595 reactions). For calculations involving the perfect inhibitor [9], the reactions for the perfect inhibitor (listed in Table 1) are added to the GRI-Mech 1.2.

A stoichiometric, freely-propagating premixed CH_4/air flame is perturbed in temperature bands of Δ = 300 K. Four types of perturbation are used:

1) reduction of chain branching by $H+O_2 \leftrightarrow OH+O$ (referred to as "$H+O_2$" below), because it provides a majority of the chain branching at high temperature,
2) reduction of heat release by $CO+OH \leftrightarrow CO_2+H$ (referred to as "CO+OH" below), because of its importance in determination of the final flame temperature,
3) catalytic scavenging of radicals (O, OH, and H) by a perfect inhibitor [9], to investigate the sensitivity of the flame to an ideal inhibitor (described below),
4) inhibition by CF_3Br, because it is used as a benchmark in flame inhibition studies.

Selected input parameters and calculated results for the flames simulated in this paper are listed in Table 2. For the $H+O_2$ and CO+OH perturbation, the reaction of interest is unaffected outside the band (B_i=1), and damped inside the band (B_i=0.45 for $H+O_2$, B_i=0.1 for CO+OH). The constants in the smoothing function are a=0.55, b=0.45, c=60, d=57. For the perfect inhibitor, reactions involving the perfect inhibitor are turned *off* outside the band (B_i=0), and turned *on* inside the band (B_i=1). The constants in the smoothing function are a=0.5, b=0.5, c=60, d=57. The mole fraction of the perfect inhibitor in the unburned gas is $4.0 \cdot 10^{-5}$, which results in a flame speed (S_L) of 27 cm/s when the inhibitor is active throughout the flame (note that S_L=41 cm/s for the uninhibited flame).

For inhibition by CF_3Br the reactants are a stoichiometric mixture of methane and air with 0.755% CF_3Br added, resulting in a one-third reduction in flame speed (to 26.4 cm/s) when the inhibitor is active throughout the flame. While the amount of inhibitor which produces a one-third reduction of flame speed is less than that typically used to suppress fires, this perturbation to the flame is adequate for demonstrating the technique. Ideally, when calculating the band sensitivity, the reactions involving Br- and F-containing species would be turned on (B_i =1) in the band and turned off outside the band (B_i=0). Because of convergence problems compounded by the size of the mechanism, we use $B_i = 10^{-4}$ for the halogen chemistry outside the band. This incomplete deactivation, when applied throughout the flame, yields a flame speed of 39.0 cm/s, due to the physical effects of the CF_3Br.

Table 1: Chemical kinetic mechanism for Perfect Inhibitor [9]. $k = A\ T^n \exp(-E_a / (R\ T))$. "In" is the inhibitor molecule. Units for k are cm, mole, s.

Reaction	A	n	E_a / R
$In+H \rightarrow InH$	10^{14}	0.0	0.0
$H+InH \rightarrow H_2+In$	10^{14}	0.0	0.0
$OH+InH \rightarrow In+H_2O$	10^{14}	0.0	0.0
$O+InH \rightarrow In+OH$	10^{14}	0.0	0.0
$In+O \rightarrow InO$	10^{14}	0.0	0.0
$H+InO \rightarrow OH+In$	10^{14}	0.0	0.0
$OH+InO \rightarrow In+HO_2$	10^{14}	0.0	0.0
$O+InO \rightarrow In+O_2$	10^{14}	0.0	0.0
$In+OH \rightarrow InOH$	10^{14}	0.0	0.0
$H+InOH \rightarrow H_2O+In$	10^{14}	0.0	0.0
$OH+InOH \rightarrow In+H_2O_2$	10^{14}	0.0	0.0
$O+InOH \rightarrow In+HO_2$	10^{14}	0.0	0.0

Table 2: Input parameters and calculated temperatures and flame speed for the flames simulated in this paper.

Perturbation	ϕ	B_i Inside band	B_i Outside band	Inhibitor mole fraction	T_{max} (K)	$S_{L,0}$ [a] (cm / s)	$S_{L,all}$ [b] (cm / s)	$S_{L,min}$ [c] (cm / s)	T_c for $S_{L,min}$ (K)
$H+O_2$	0.7	0.45	1.0	n.a.	1850	20.7	n.c.	15.5	1550
$H+O_2$	1.0	0.45	1.0	n.a.	2235	41.2	n.c.	31.0	1800
$H+O_2$	1.3	0.45	1.0	n.a.	2056	25.2	n.c.	18.0	1850
CO+OH	1.0	0.1	1.0	n.a.	2235	41.2	n.c.	29.1	1850
Perfect	1.0	1.0	0.0	$4.0 \cdot 10^{-5}$	2235	41.2	27	30.9	1950
Perfect	0.7	1.0	0.0	$2.0 \cdot 10^{-5}$	1850	20.7	13.8	16.2	1650
Perfect	1.3	1.0	0.0	$2.6 \cdot 10^{-5}$	2056	25.2	16.8	18.3	2000
CF_3Br	1.0	1.0	10^{-4}	0.00755	2235	41.2 [d]	26.4	29.2	1750

Notes:
[a] Flame speed of the unperturbed or uninhibited flame
[b] Flame speed with perturbation throughout flame
[c] Minimum flame speed with perturbation in a 300 K band
[d] The flame speed is 39.0 cm / s when the halogen chemistry is turned off throughout the flame because of the physical effects of CF_3Br
n.a. = not applicable
n.c. = not calculated

RESULTS AND DISCUSSION

Figure 3 shows the response of the flame to each of the perturbations. The reduction in flame speed for $H+O_2$ and CO+OH can only be compared qualitatively to results for the perfect inhibitor and CF_3Br, because of the different shapes of the bands. The minimum flame speed occurs at band-center temperature (T_c) of 1800 K for $H+O_2$, 1850 K for CO+OH, 1950 K for the perfect inhibitor, and 1750 K for CF_3Br. Using reaction flux analysis, it is possible to infer that perturbations at these temperatures would most strongly affect the flames. For $H+O_2$ and CO+OH, these temperatures correspond to the maximum reaction rate of the affected reaction (as shown in Figure 4). Likewise, for the perfect inhibitor the temperature is near the temperature of peak mole fractions of O, H and OH (as shown in Figure 3). With the band sensitivity technique, however, it is not necessary to speculate on the change in the flame speed that would caused by a perturbation in part of the flame, and we directly obtain quantitative information about the influence of the perturbations on flame speed.

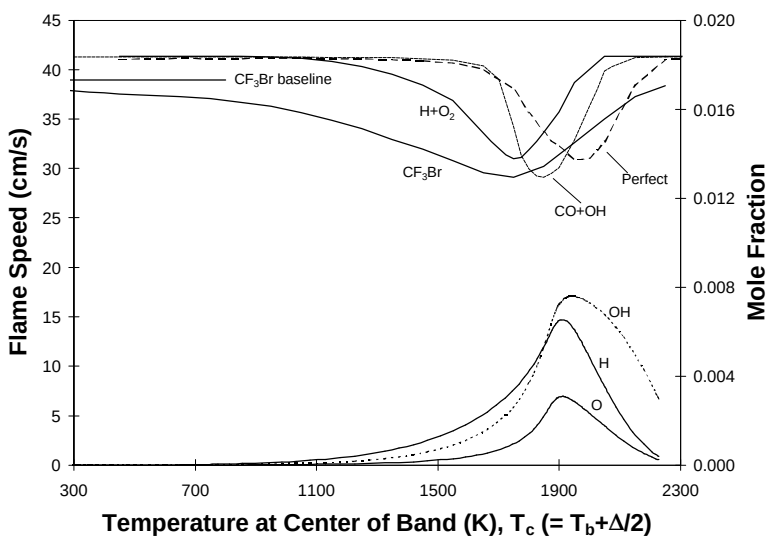


Figure 3: Variation of flame speed for four types of perturbation (left axis): reduction of $H+O_2 \leftrightarrow OH+O$ reaction rate, reduction of the $CO+OH \leftrightarrow CO_2+H$ reaction rate, the perfect inhibitor and CF_3Br. The "CF_3Br baseline" refers to the flame speed when the halogen chemistry is damped by 10^{-4}. Δ = 300 K, so the band extends 150 K below and above the temperature shown on the x-axis. Also shown are calculated mole fraction of OH, H, and O in an uninhibited stoichiometric methane-air flame (right axis).

The location of the maximum reduction in flame speed is strongly affected by the kinetics and thermodynamics of the inhibiting species. Whereas the perfect inhibitor remains active throughout the flame, CF_3Br loses its effectiveness as the equilibrium constant for the inhibition reactions (e.g., $H+HBr \leftrightarrow H_2+Br$) shifts at higher temperature. CF_3Br has a lower temperature of peak effectiveness because at high temperature the inhibiting reaction $H+HBr \rightarrow H_2+Br$ is slower than the reverse $H_2+Br \leftrightarrow H+HBr$.

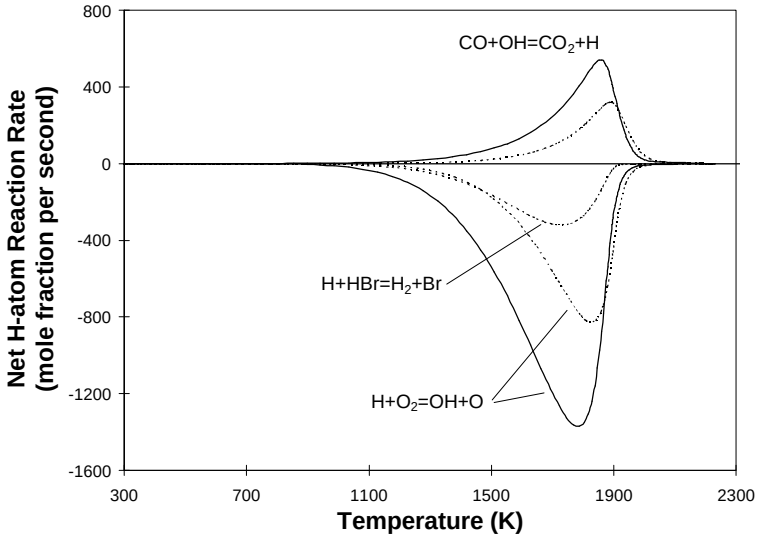


Figure 4: Net H-atom reaction rate for three important reactions. Solid lines correspond to an uninhibited stoichiometric methane-air flame (for CO+OH ↔CO_2+H and H+O_2↔OH+O), and dashed lines correspond to a stoichiometric methane-air flame with 0.755% CF_3Br added.

In earlier studies of inhibition of premixed flames by CH_3Br [16], CF_3Br [17] and HBr [18], it was argued that the primary inhibition occurs upstream of the main reaction zone. Wilson [16] and Wilson et al. [17] investigated inhibition of low pressure (0.05 atm) methane-oxygen flames inhibited by CH_3Br and HBr. Based on flame structure measurements and calculations, they suggested that inhibition occurred through reduction of radical generation in the "pre-ignition" part of the flame. In a numerical modeling study, Westbrook [18] argued that HBr has its maximum effect in a temperature range between about 1000 and 1400 K, which is upstream of the main reaction zone. While our results also show that some of the inhibition effect of HBr and CF_3Br occurs upstream of the locations of the maximum rates for the chain branching and heat release reactions, the temperature region of greatest influence that we obtain is somewhat higher (1600-1900 K) than argued in ref. [18].

Now we return to the H+O_2 perturbation and perfect inhibitor and discuss results for different equivalence ratios. We seek to determine if rich and lean flames are affected differently by the perturbations than stoichiometric flames. Figure 5 shows the effect of chain branching perturbation (Δ=300 K) on *normalized* flame speed for three equivalence ratios: lean (ϕ = 0.7), stoichiometric (ϕ = 1.0), and rich (ϕ = 1.3). Table 2 lists calculated maximum temperature and flame speed for uninhibited flames at each equivalence ratio. The normalized flame speed is defined as the ratio of the flame speed of a band-inhibited flame to the flame speed of the corresponding uninhibited flame. The temperature of minimum flame speed of the different flames follows the relative position peak of the H-atom mole fraction (see Figure 6a). For flames of differing stoichiometry, comparisons of the temperature regime for the maximum effect of H+O_2 inhibition are confounded by differences in the final temperature (see Table 2).

Furthermore, the magnitude of reduction in flame speed at each equivalence ratio should not be compared because the 300 K band spans a different fraction of the flame for each stoichiometry because of the different final temperatures.

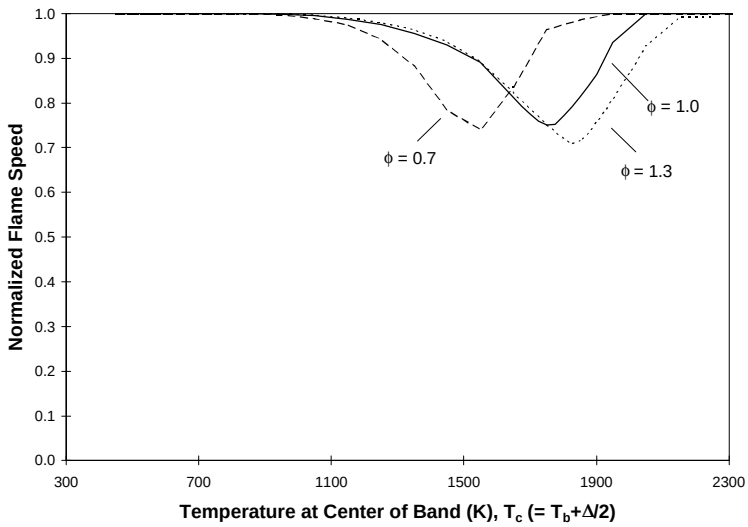


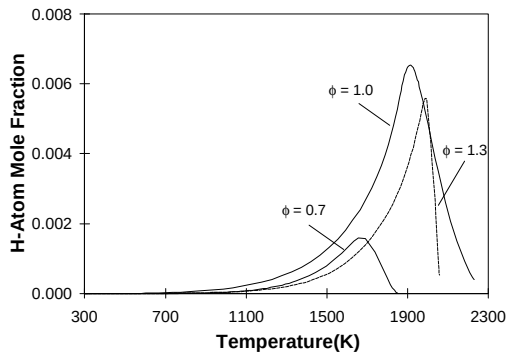
Figure 5: Effect of the location of chain branching inhibition on normalized flame speed for 3 equivalence ratios.

The *relative* positions of the maximum effect of the perturbation can be compared by plotting the results of Figure 5 with a normalized temperature as the independent variable. Figure 7 shows that the stoichiometric flame is affected at the lowest normalized temperature, which can be explained by the relative position of the peak H-atom mole fraction (see Figure 6a).

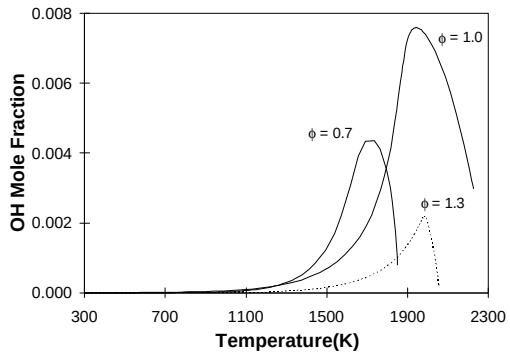
The flame speeds for stoichiometric, rich and lean flames inhibited by the perfect inhibitor are shown in Figure 8. The initial mole fraction of perfect inhibitor is the amount needed for a 1/3 reduction of flame speed (with the inhibiting reactions active throughout the flame) from the uninhibited condition (see Table 2). For band inhibition at the three values of ϕ, the perfect inhibitor shows flame speed reductions qualitatively similar to the results for $H+O_2$ suppression: the temperature range for maximum effect is lowest for the lean flame, and is higher and nearly the same for stoichiometric and rich flames. The ordering follows that of the peak radical mole fractions that are shown in Figure 6a-c. The calculations generally show that inhibition in only a small portion of the flame can have a large effect. For example, as shown in Figure 8, if the inhibiting reactions are turned on between 1500 and 1800 K, the reduction in flame speed is 60-80% as much as when the inhibiting reactions are turned on everywhere.

A common result of the calculations presented here for the perfect inhibitor is that perturbation near the region of high radical mole fraction has the strongest effect on flame speed. In other words, removing H atoms from the high temperature region *before* they can diffuse upstream has the strongest effect on flame speed because

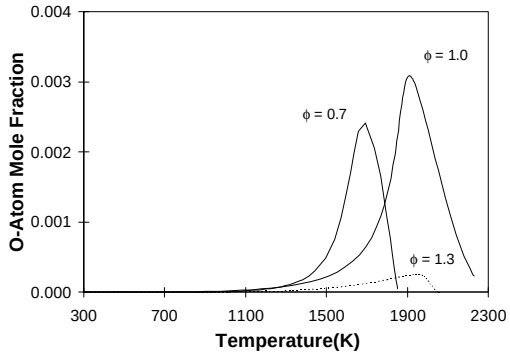
inhibition reactions are faster in regions of high radical mole fraction and high temperature. The results for CF_3Br show, however, that the thermodynamics and kinetics of the inhibitor can be important (due to shifting partial equilibrium at high temperature).



a)



b)



c)

Figure 6: Calculated mole fraction profiles for H, OH and O in uninhibited methane-air flames for three stoichiometric ratios. a) H-atom, b) OH, c) O-atom.

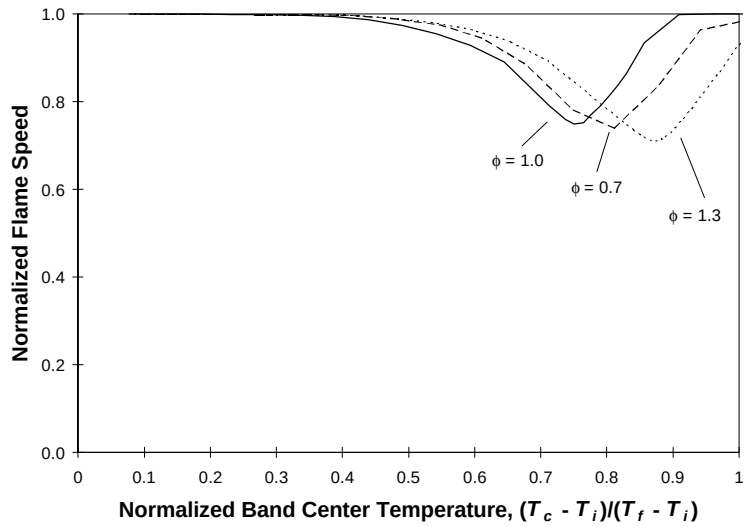


Figure 7: Normalized flame speed variation versus normalized temperature. T_c is the band center temperature, T_i is the initial reactant temperature, and T_f is the maximum temperature.

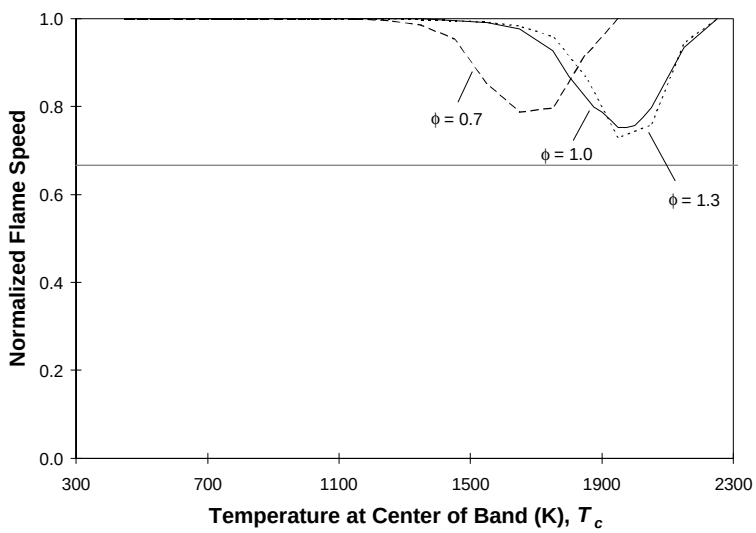


Figure 8: Effect of the location of perfect inhibition on normalized flame speed for 3 equivalence ratios. The horizontal line marks the normalized flame speed when the flames are inhibited throughout the flame.

Sudden Activation or Deactivation of a Chemical Inhibitor

Potentially effective new fire suppressants may involve an agent that is inert and non-toxic at storage temperature, and releases an effective fire suppressant when added to a fire (via decomposition or evaporation). To simulate such a system, we use the band sensitivity method with a band that is shaped like a step function (as opposed to the pulse shape of the previous section). The shape of the B_i function is illustrated in Figure 2-c. Below the "activation temperature" the inhibition reactions are turned off,

and above the activation temperature the inhibition reactions are turned on. For ease of calculation, we use the perfect inhibitor model (with inhibitor mole fraction of $4.0 \cdot 10^{-5}$). Although these calculations of inhibitor activation are highly idealized, they provide insight into chemical inhibition of premixed flames. The curve labeled "activation" in Figure 9 shows the flame speed resulting from inhibitor activation at different temperatures between 300-2200 K. The flame speed is fairly constant up to about 1700 K, but then starts to increase. The location of the increase is coincident with the steeper rise in radical concentration. As the activation occurs later in the flame, the inhibitor has less time to scavenge radicals.

Another interesting situation is an inhibitor that suddenly decomposes to an inactive species. We simulate this with a band in which the B_i function is a mirror image of the previous example, and is illustrated in Figure 2-d. Above the "deactivation" temperature the inhibition reactions are turned off, and below the deactivation temperature the inhibition reactions are turned on. As in the sudden activation calculations, the effect of the inhibitor is more or less constant until about 1700 K. The very small reduction in flame speed when the inhibitor is active between 300 and 1700 K reaffirms the importance of the high temperature reactions. The most important region for the perfect inhibitor is above 1700 K for a strong effect on the flame speed.

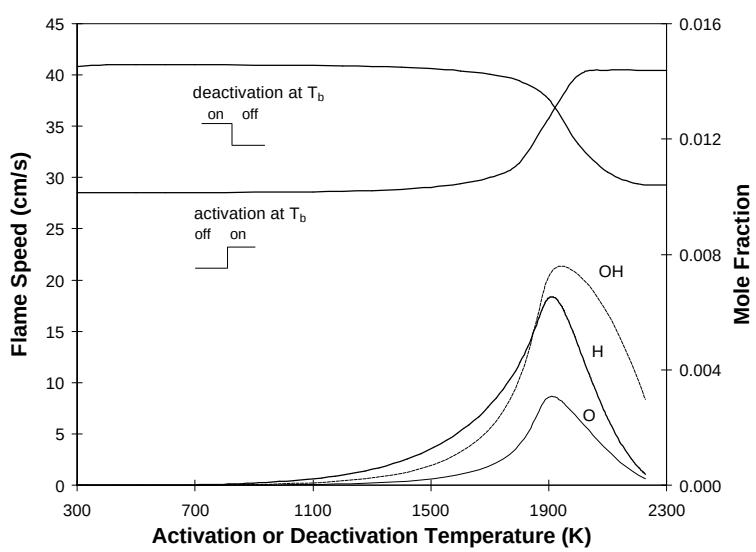


Figure 9: Variation of flame speed for sudden inhibitor activation (Figure 2-c) or sudden inhibitor deactivation (Figure 2-d) for a stoichiometric methane-air mixture. The perfect inhibitor mole fraction is $4.0\ 10^{-5}$. Also shown are calculated mole fraction of OH, H, and O in an uninhibited stoichiometric methane-air flame.

CONCLUSION

A brute-force sensitivity technique that involves localized perturbation of reaction rate has been presented. The technique can be used to investigate the sensitivity of a flame to reactions proceeding in different zones. Additionally, it allows researchers to ask

"what if?" questions about flame inhibitors with limited information about the inhibition kinetics. The technique is used to investigate the sensitivity of a premixed flame to several different chemical perturbations. The results indicate that the flame speed of a stoichiometric CH_4/air premixed flame is most reduced when the perturbation is near the regions of maximum radical mole fraction and maximum reaction rates of the perturbed reactions. Calculations of CF_3Br-inhibited flames find a temperature of maximum influence that is higher than previous suggestions for Br-based inhibitors [18]. Each of the perturbations have a negligible effect in the region of the flame below 1200 K.

For perturbation of the $H+O_2 \leftrightarrow OH+O$ reaction rate and addition of the perfect inhibitor, the temperature of minimum flame speed of the lean (ϕ=0.7), rich (ϕ=1.3), and stoichiometric (ϕ=1.0) flames follows the relative position peak of the H-atom mole fraction. The *relative* temperatures of the maximum effect of the perturbation shows that the stoichiometric flame is affected at the lowest normalized temperature, which can be explained by the relative position of the peak H-atom mole fraction. The calculations with the perfect inhibitor show that inhibition in a fraction of the flame can cause a significant reduction in flame speed. In some cases, inhibition in only 300 K of the flame causes nearly as much reduction in flame speed as when the inhibiting reactions are turned on everywhere.

Sudden activation and deactivation of the perfect inhibitor are simulated in a stoichiometric flame. In both cases, the effect of the inhibitor is small when the activation or deactivation temperature is below 1700 K.

In future research, we will use the band sensitivity technique with larger perturbations, different suppressants, different fuels and conduct similar calculations in diffusion flames.

The authors thank Dr. D. Burgess for his insightful comments and suggestions.

REFERENCES

[1] Williams, F.A., *Combustion Theory*, Benjamin/Cummings Publishing Company, Menlo Park, California, 1985.

[2] Westbrook, C.K. and Dryer, F.L., "Chemical Kinetic Modeling of Hydrocarbon Combustion", *Prog. Energy Combust. Sci.* 10: 1 (1984).

[3] Olsson, J.O. and Andersson, L.L., "Sensitivity Analysis Based on an Efficient Brute-Force Method, Applied to an Experimental CH_4/O_2 Premixed Laminar Flame", *Combustion and Flame* 67(2) 99-109 (1987).

[4] Warnatz, J., "Structure of Laminar Alkane-,Alkene-, and Acetylene Flames", *Eighteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1980, pp. 369-384.

[5] Teets, R.E. and Bechtel, J.H., "Sensitivity Analysis of a Model for the Radical Recombination Region of Hydrocarbon-Air Flames", *Eighteenth Symposium*

(International) on Combustion, The Combustion Institute, Pittsburgh, 1980, pp. 425-432.

[6] Smooke, M.D., Rabitz, H., Reuven, Y., Dryer, F.L., "Application of Sensitivity Analysis to Premixed Hydrogen-Air Flames", *Combustion Science and Technology* 59: 295-319 (1988).

[7] Warnatz, J., "Resolution of Gas Phase and Surface Combustion into Elementary Reactions", *Twenty-Fourth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1992, pp. 553-579.

[8] Frenklach, M., "Modeling", in *Combustion Chemistry*, (W.C. Gardiner, Jr., Ed.), Springer-Verlag, New York, 1984, pp. 423-453.

[9] Babushok, V., Tsang, W., Linteris, G.T., and Reinelt, D., "Chemical Limits to Flame Inhibition", accepted for publication in *Combustion and Flame*, 1998.

[10] Kee, R.J., Grcar, J.F., Smooke, M.D., and Miller, J.A., *A Fortran Computer Program for Modeling Steady Laminar One-dimensional Premixed Flames*, Sandia National Laboratories Report SAND85-8240, 1991.

[11] Kee, R.J. Rupley, F.M., and Miller, J.A., CHEMKIN-II: A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics, Sandia National Laboratory, SAND89-8009B, 1989.

[12] Kee, R.J., Dixon-Lewis, G., Warnatz, J., Coltrin, R.E, and Miller, J.A., A Fortran Computer Package for the Evaluation of Gas-Phase, Multicomponent Transport Properties, Sandia National Laboratory, SAND86-8246, 1986.

[13] NIST XSenkplot: An Interactive, Graphics Postprocessor for Numerical Simulations of Chemical Kinetics, *http://www.nist.gov/cstl/div836/xsenkplot*

[14] Frenklach, M., Wang, H., Yu, C.-L., Goldenberg, M., Bowman, C.T., Hanson, R.K., Davidson, D.F., Chang, E.J., Smith, G.P., Golden, D.M., Gardiner, W.C., and Lissianski, V., GRI-Mech 1.2, http://www.me.berkeley.edu/gri_mech.

[15] Noto, T., Babushok, V., Burgess, D.R., Hamins, A., Tsang, W., and Miziolek, A., *Twenty-Sixth Symposium (International) on Combustion*. The Combustion Institute, Pittsburgh, PA, 1996, pp. 1377-1383.

[16] Wilson, W.E., "Structure, Kinetics, and Mechanism of a Methane-Oxygen Flame Inhibited with Methyl Bromide", *Tenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1965, pp. 47-54.

[17] Wilson, W.E., O'Donavan, J.T., and Fristrom, R.M., "Flame Inhibition by Halogen Compounds", *Twelfth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1969, pp. 929-942.

[18] Westbrook, C.K., "Inhibition of Methane-Air and Methanol-Air Flames by HBr", *Combustion Science and Technology* 23: 191-202 (1980).