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Is CF_3Br Representative of Efficient Fire Suppressants?

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ABSTRACT

CF_3Br (Halon 1301) is often used as a standard for measuring the effectiveness of chemical fire suppressants, since its inhibition properties have been known for many years, and the chemical kinetics relevant to its suppression of combustion have been extensively studied. Because of the phaseout of CF_3Br due to its contribution to the depletion of stratospheric ozone, new classes of efficient fire suppressants must be identified. In recent years, CF_3Br has been extensively studied, although its manufacture has been prohibited in developed countries since 1994. One issue not often addressed is whether CF_3Br is "typical" of efficient fire suppressants in general. To this end, we have modeled premixed flames containing representative inhibitors of various types, including inert gases, fluorocarbons, and catalytic scavengers of flame radicals. Calculations show that although CF_3Br is itself a catalytic scavenger, its effect on flame structure and burning velocity is in many respects more similar to that of the noncatalytic hydrofluorocarbons than to other catalytic scavengers such as iron and sodium. Details of the suppression behavior of CF_3Br and other representative compounds support the conclusion that in many combustion environments, knowledge of the behavior of CF_3Br is not necessarily relevant to gaining understanding of efficient fire suppressants in general.

INTRODUCTION

CF_3Br is often used as a benchmark for other chemical fire suppressants, since its inhibition properties have been known for many years, and the chemical kinetics relevant to its suppression of combustion have been extensively studied. Because of the phaseout of CF_3Br due to its contribution to the depletion of stratospheric ozone, new classes of efficient fire suppressants must be identified. In recent years, CF_3Br has been studied both experimentally and computationally, although its manufacture has been prohibited in developed countries since 1994, with the ban scheduled to take effect worldwide by 2005.

One issue which has not generally been considered is whether CF_3Br is "typical" of efficient fire suppressants in general. In other words, will all promising replacements for CF_3Br have properties which are "similar" in some respect? Is commonality of properties with CF_3Br a useful guide in the search for environmentally acceptable alternatives? To this end, we have performed modeling studies of premixed flames containing substances representative of different classes of inhibitors, including inert gases, fluorocarbons, and catalytic scavengers of flame radicals.

TYPES OF SUPPRESSANTS

Suppressants may be grouped into various categories. Physical suppressants (such as nitrogen, argon, CF_4, and water) do not participate in flame chemistry to a significant extent and inhibit combustion by adding heat capacity and diluting the reactants. Chemical suppressants also participate in the flame chemistry and may be subdivided into two groups: catalytic suppressants (including bromine, iodine, and various metallic elements) reduce concentrations of flame radicals through a regenerative cycle (one molecule of suppressant can recombine several radicals). Noncatalytic suppressants (e. g. fluorocarbons) also reduce concentrations of flame radicals by scavenging flame radicals, at least in certain regions of the flame, but do not exhibit a catalytic cycle and are generally less effective. CF_3Br is primarily a catalytic suppressant [1], due to an H + H recombination cycle involving the bromine atom, although the CF_3 moiety adds some noncatalytic suppression as well.

The effectiveness of an inhibitor may be placed on a quantitative basis by considering an "inhibition parameter" Φ first proposed by Rosser *et al.* [2] and modified by Noto *et al.* [3]:

$$\Phi = \ln(U_0/U_i) \times (X_{O2}/X_i) \qquad (1)$$

where U_0 and U_i are the burning velocities of the uninhibited and inhibited flames, respectively, and X_{O2} and X_i are the reactant mole fractions of oxygen and inhibitor. In ref. [3] the burning velocity of a given fuel/air mixture was shown to exhibit an exponential dependence on the inhibitor concentration. This exponential dependence, by which the inhibition parameter was defined, was shown to hold for the inert agents N_2 and CF_4, several hydrofluorocarbons, and CF_3Br. Since catalytic scavengers intrinsically exhibit saturation effects (the concentrations of flame radicals, which typically exist in superequilibrium, cannot be reduced below the thermal equilibrium values at the local flame temperature) the existence of a similarity relation describing inhibition by CF_3Br as well as noncatalytic agents is somewhat unexpected. Saso *et al.* [4] modeled the combined effect of CF_3Br/inert inhibitors and found synergism (the two agents in combination had a greater inhibiting effect than the additive effect of the agents in isolation). The behavior was attributed to a temperature effect on the inhibition effectiveness of CF_3Br, rather than a saturation phenomenon. Over a range of adiabatic flame temperatures, Saso *et al.* found CF_3Br to have virtually identical inhibition parameters at concentrations of 0.5% and 1% in methane/oxygen/inert mixtures, once again suggesting the absence of significant saturation effects.

MODELING RESULTS: BURNING VELOCITIES AND SPECIES PROFILES IN INHIBITED PREMIXED FLAMES

In the calculations described below, the PREMIX code [5] was used to compute burning velocities and flame structures of atmospheric pressure flames. An 85 cm domain was used in the calculations. Comparison with thermal equilibrium calculations showed that at the final grid point, temperatures were generally within 5K and radical concentrations within a few percent of their equilibrium values. Flames were stoichiometric, atmospheric pressure methane/oxygen, with various inhibitors added as indicated below.

For the hydrocarbon chemistry, GRIMech2.11 was used as the kinetic mechanism. Fluorocarbon chemistry was based on mechanism refinement previously performed in our laboratory [6,7]. Bromine chemistry used for CF_3Br was that developed by Noto et al. [4]. The kinetic mechanism for sodium was based on that of Zamansky *et al.* [8], while that for $Fe(CO)_5$ was described by Rumminger and Linteris [9].

In Figs. 1-3, changes in burning velocity, adiabatic flame temperature, radical superequilibrium, as well as the inhibition parameter Φ as defined by Noto *et al.*, are plotted as a function of inhibitor concentration. Note that a constant value of Φ indicates that the exponential dependence of flame speed on inhibitor concentration is well observed. The three plots compare the changes in the flame structure caused by CF_3Br with that of nitrogen (an inert agent) and sodium hydroxide (a catalytic agent). Nitrogen has a modest inhibition parameter (approximately 0.5) nearly independent of its concentration. The adiabatic flame temperature must be lowered by nearly 300K for the burning velocity to be reduced by 50%. While the peak concentrations of the flame radicals H, O, and OH decrease as the flame is inhibited, the peak concentrations normalized by the equilibrium values at the adiabatic flame temperature increase. This phenomenon provides a basis for the synergy observed between a catalytic and a physical agent, since a flame inhibited by a physical agent has a greater radical superequilibrium which the catalytic agent can exploit.

In the flame inhibited by NaOH, by contrast, the flame speed is reduced by 50% with virtually no change in the adiabatic temperature. The radical superequilibrium is drastically reduced as the inhibitor is added, eventually reaching unity for all primary flame radicals for a sufficiently large inhibitor concentration (meaning that the radical concentrations never overshoot their equilibrium values). Most notably, the inhibition parameter is not constant as a function of inhibitor concentration, but varies by more than a factor of three over the range of sodium concentrations considered here. The similarity relationship identified by Noto *et al.* does not hold for sodium.

For inhibition by CF_3Br, the flame speed is again reduced with little change in the adiabatic temperature (about 30K for the range of concentrations shown in the plot). The degree of radical superequilibrium is reduced with increasing agent concentration, though not as dramatically as for sodium. By both of these measures, CF_3Br shows behavior typical of catalytic agents. The inhibition parameter, unlike for sodium, is nearly constant as a function of inhibitor concentration (except for the initial data point at an inhibitor concentration of 0.1% which has a high uncertainty due to the small differences in flame speeds). This nearly constant inhibition parameter was found by Noto *et al.* although the modifications to the fluorocarbon kinetics yield somewhat higher inhibition parameters, in excellent agreement with the experimental value of 14.0 [4].

This raises the question of why the exponential relationship between burning velocity and inhibitor concentration is observed for CF_3Br but not for other chemical inhibitors. The present results support the conclusion of Saso *et al.* that saturation is a minor effect in the suppression effectiveness of CF_3Br/inert mixtures. One point is that for inhibition by CF_3Br, the H atom superequilibrium is only reduced by some 30% for a 50% reduction in flame speed, whereas for NaOH the H atom superequilibrium is reduced by nearly 80% for the same reduction in flame speed. Thus saturation is not as pronounced for CF_3Br in part because the peak radical concentrations are still far out of equilibrium even when the burning velocity has been substantially reduced.

The other important point for CF_3Br is that the bromine catalytic cycle involves the sequence of reactions [10]

$$Br + Br + M \Rightarrow Br_2 + M \qquad (1)$$

$$H + Br_2 \Rightarrow HBr + Br \qquad (2)$$

as an important pathway in regeneration of HBr, since the direct reaction

$$H + Br + M \Rightarrow HBr + M \qquad (3)$$

has rather slow kinetics. This has two consequences: the increasing importance of Reaction (1) (since it has a second order dependence on the inhibitor concentration) compensates for the saturation effect as the inhibitor concentration is increased. Also, a much higher concentration of bromine is required for this reaction to be significant. Compared to sodium and iron, whose suppression kinetics are not thought to depend significantly on any second order pathways, bromine is a relatively inefficient scavenger.

COMBINED EFFECTS OF MIXTURES OF AGENTS

Since various studies have described synergism of combinations of CF_3Br and inert agents, it is worth exploring to what extent the observations carry over to other combinations of agents. Furthermore, is there any advantage to combining different chemical scavengers which act independently (i. e. recombine different flame radicals)?

To this end, inhibition by iron was modeled in combination with both nitrogen and sodium. For this modeling, iron was considered to participate in a three step mechanism involving only O + O recombination. This pathway was identified by Rumminger and Linteris [9] but is usually secondary in importance to an H + H recombination pathway. Using this simplified model, sodium and iron do not directly compete for the same flame radicals, since sodium primarily undergoes an H + OH recombination cycle. This model is *not* intended as an accurate description of iron's combustion chemistry but to investigate the combined effect of scavengers which operate through different pathways.

In Table 1, the effects of iron and sodium both separately and in combination, are listed. The effectiveness of the inhibitors when combined are described by their "differential inhibition parameters." The differential inhibition parameter of substance A is determined by comparing the burning velocity of a mixture inhibited by A and B in combination, to that of the mixture inhibited by B alone. As seen in the Table, the differential inhibition parameters of iron and sodium in combination are much less than those of the two elements taken separately. Even though the two elements do not directly compete for the same flame radicals, the rapid exchange between H, O, and OH means that the two suppressants reduce each other's effectiveness.

Iron, in combination with nitrogen, does exhibit synergy. Figure 4 shows the burning velocity, flame temperature, and differential inhibition parameter of iron (using the O + O recombination mechanism) as a function of nitrogen addition to a methane/air mixture. The differential inhibition parameter of 500 ppm FeO_2 increases by some 23% as the flame temperature is lowered by nitrogen addition from 2230K to 2010K. These results may be compared to those of Saso *et al*. [4], who found that the inhibition parameter of CF_3Br increased by some 45% (at both 0.5% and 1.0% mole fractions of agent) over the same range of final flame temperatures. While the findings of synergism agree qualitatively, the final flame temperature influences the inhibition parameter of CF_3Br twice as much as that of the O + O recombination cycle of iron. Therefore while synergism in catalytic/inert mixtures may be a general characteristic, its magnitude can vary considerably depending on the kinetics of the catalytic component.

CORRELATION OF BURNING VELOCITIES, FINAL FLAME TEMPERATURE, AND RADICAL CONCENTRATIONS

According to laminar flame theory, the burning velocity of a premixed flame is proportional to the square root of the overall reaction rate. In modeling the burning velocity of a large number of inhibited flames, the burning velocity correlates in almost all cases with the product of the peak H atom mole fraction and a global activation energy:

$$S_L^2 = A^2 X_H \exp(-E_a/kT_f). \qquad (2)$$

where S_L is the laminar burning velocity, X_H the peak mole fraction of atomic hydrogen, and T_f the final flame temperature. The fitted parameters A and Ea, obtained by considering the flame inhibited by nitrogen, are A=7940 cm/s, E_a=24.7 kcal/mol. The same empirical correlation holds for inhibition by other inert gases, by iron and sodium, by nitrogen and iron in combination (Fig. 4), and by artificially increasing the H + OH recombination rate. For the catalytic agents, which do not cause appreciable changes in the final flame temperature, the flame speed correlates with the peak mole fraction of atomic hydrogen, but not with that of atomic oxygen or OH radicals.

The observation that atomic hydrogen controls the burning velocity is not unexpected, due to the high diffusivity and reactivity of this species. Nevertheless, some noteworthy conclusions can be made: 1) this correlation can quantitatively describe the effect of a wide variety of inhibitors, both individually and in combination; 2) catalytic agents reduce the flame speed by reducing the atomic hydrogen concentration, whether or not the scavenging cycle directly involves H atom recombination. The partial equilibrium between H, O, and OH is not disrupted in most inhibited flames.

Table 2 compares the burning velocities estimated using Eqn. (2) to the calculated values for a variety of flame inhibitors. In almost all cases, the reduction in burning velocity relative to the uninhibited flame, predicted by Eqn (2) is within 10% of the actual value using the full kinetics. This relationship between burning velocity, final flame temperature, and peak H atom mole fraction holds for many agents (both catalytic and inert) and also when one artificially increases the H + OH recombination rate. At the same time, there are a few notable exceptions: the fluorocarbons CHF_3 and C_3HF_7 are much better inhibitors (by nearly a factor of two) than Eqn (2) would predict. So are both CF_3Br and HBr. Flame structure modeling indicates that the breakdown of this relationship involving the peak H atom concentration is a consequence of these agents reducing the H atom concentration mostly in the early part of the flame, as demonstrated below.

CHANGES IN FLAME STRUCTURE DUE TO DIFFERENT AGENTS

The explanation for why the correlation between flame speed, H atom concentration, and temperature does not hold for either fluorocarbons or bromine containing compounds can be gained from examination of these compounds' effects on flame structure. In Fig. 5 the mole fraction of atomic hydrogen is plotted against the local temperature for flames inhibited by the inert agent N_2, the catalytic agent $Fe(CO)_5$, the noncatalytic fluorocarbon CF_3CHFCF_3, and CF_3Br. All the inhibited flames have burning velocities approximately 50% that of the uninhibited flame, whose structure is also plotted for comparison. For all the flames considered here, temperature overshoot does not occur; the temperature monotonically increases with position passing from reactants to products.

The way in which the relationship between H atom mole fraction and local temperature is altered is characteristic of each type of agent. Other agents modeled (not shown on the plot for clarity) produce H atom profiles which closely resemble each other within the same class: CF_4 and N_2, NaOH and $Fe(CO)_5$, CH_2FCF_3 and CF_3CHFCF_3. The physical agents reduce the final flame temperature, but the H atom mole fraction at a given isotherm (above approximately 1300K) is changed very little from its value in the uninhibited flame. Both iron and sodium reduce the H atom mole fraction by a relatively constant factor throughout the reaction zone, in other words the inhibition occurs throughout the flame. The fluorocarbons, on the other hand, reduce the H atom mole fraction early in the flame (in the region below about 1200K) but have relatively little impact on the peak concentration. The same situation occurs for CF_3Br, in this respect CF_3Br bears more resemblance to nonbrominated fluorocarbons than it does to other catalytic agents such as iron and sodium.

The depletion of radical species early in the flame has a marked influence on the flame speed. It is for this reason that fluorocarbons and bromine compounds are better inhibitors than the changes in temperature and peak H atom concentrations would predict. This observation implies that agents which deplete radicals in high temperature regions but not early in the flame are likely to be less effective inhibitors than would otherwise be expected. This may be the case, for instance, for condensed-phase agents which must undergo a vaporization process before inhibition chemistry can begin.

CONCLUSIONS

Is CF_3Br representative of efficient fire suppressants? The short answer is that it depends on what CF_3Br is to be used for. From a practical perspective, using CF_3Br as a benchmark makes sense, since the fire protection community has widespread experience with this agent and stating the efficiency of a proposed replacement on a relative basis to that of CF_3Br has merit. At the same time, not all other efficient suppression agents are "like CF_3Br" in either the details of their suppression chemistry or in many cases in the qualitative aspects of their behavior, particularly for condensed phase agents.

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Table 1

Inhibition by Two Chemical Agents in Combination

Flame: stoichiometric methane/air, atmospheric pressure

Agent	Flame Speed (cm/s)	Inhibition Parameter Φ [Eqn. (1)]
none	39.6	---
0.2% $(NaOH)_2$	17.0	40.1[a]
0.1% FeO_2	29.5	56.1
0.1% FeO2 + 0.2%$(NaOH)_2$	14.9	24.9(Fe), 32.4(Na)[b]

[a] per sodium atom

[b] differential effect of specified inhibitor relative to other inhibitor alone.

Table 2
Comparison of Calculated Flame Speeds to Values from Eqn. (2)

$S_{eqn} = A(X_{H,max}*\exp(-E_a/kT_{ad}))^{1/2}$ A=7940 cm/s E_a=24.7 kcal/mol

flame condition	$T_{adiabatic}$	$X_H$max	S_{premix}	S_{eqn}	$\Delta S_{premix}/\Delta S_{eqn}$[a]
CH_4/air (uninhibited)	2234	6.64e-3	39.8	39.8	---
+3.85% N_2	2187	5.96e-3	35.5	35.6	1.01
+9.09% N_2	2121	5.12e-3	30.2	30.2	1.00
+13.04% N_2	2065	4.45e-3	26.1	26.0	0.99
+16.67% N_2	2015	3.94e-3	22.6	22.7	1.01
+8.26% CF_4 (inert)	1968	3.50e-3	18.4	19.9	1.07
+500ppm FeO_2 (O+O cycle)	2220	2.52e-3	33.3	32.7	0.92
+0.5%HBr (H+H cycle)	2221	5.36e-3	30.3	35.2	2.08
+0.5%HBr (H+OH cycle)	2220	5.47e-3	33.3	35.5	1.52
+5.2%CHF_3 (phi=1.1)	2036	4.04e-3	16.3	23.7	1.46
+3%C_3HF_7 (phi=0.9)	2161	3.86e-3	17.8	27.7	1.81
+0.05% $(NaOH)_2$	2219	2.97e-3	28.0	26.2	0.87
+0.40%$(NaOH)_2$	2177	3.31e-4	9.4	8.3	0.97
increase H + OH + M rate:					
x10	2234	4.04e-3	32.0	31.1	0.90
x100	2234	1.35e-3	19.8	18.0	0.92
x1000	2234	3.64e-4	11.2	9.3	0.94

[a] $(39.8-S_{premix})/(39.8-S_{eqn})$

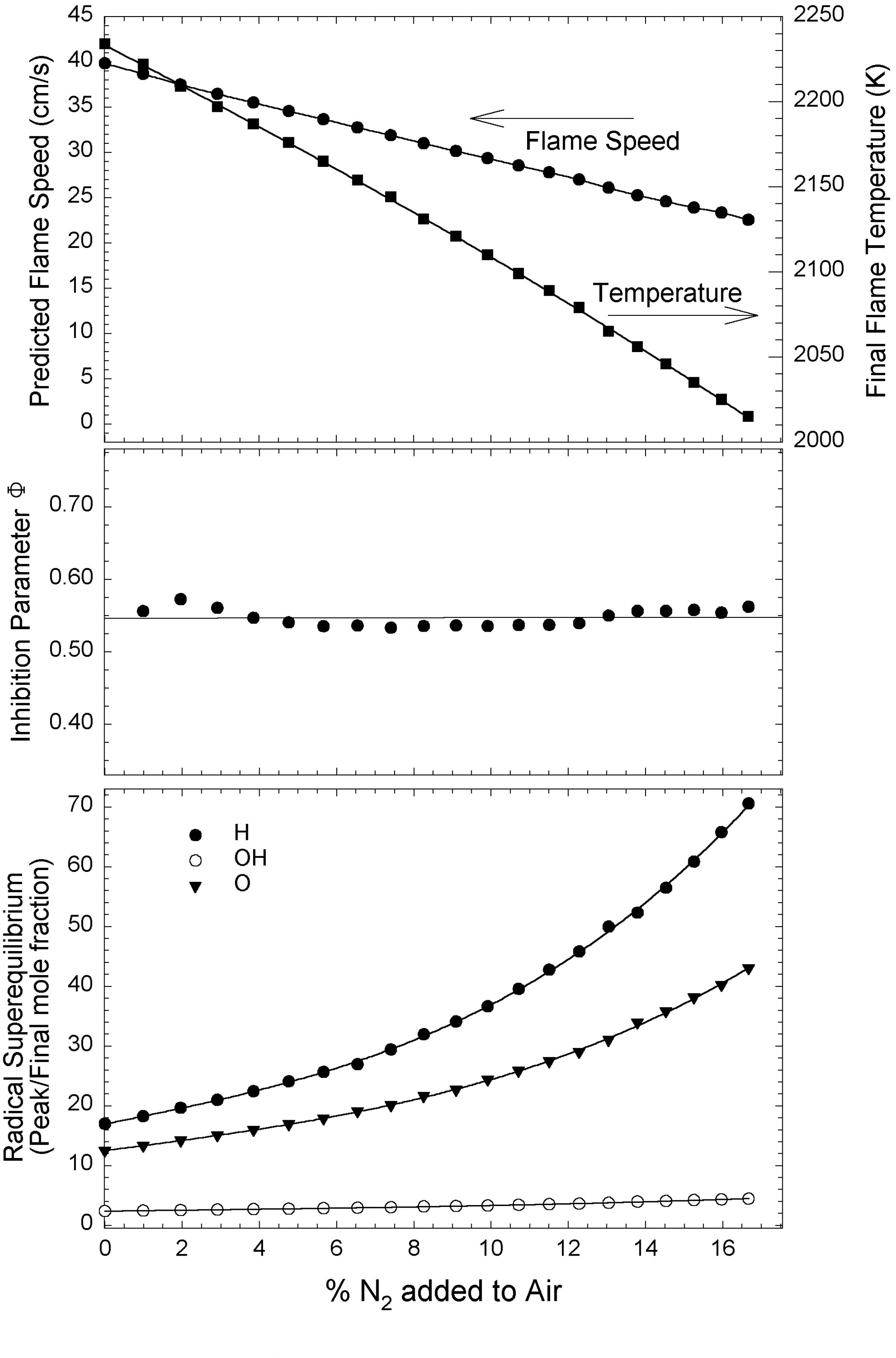

Figure 1: Flame speed, final flame temperature, inhibition parameter (defined in Ref. [3]), and superequilibrium concentrations of flame radicals computed for atmospheric pressure stoichiometric methane/air mixtures inhibited by nitrogen.

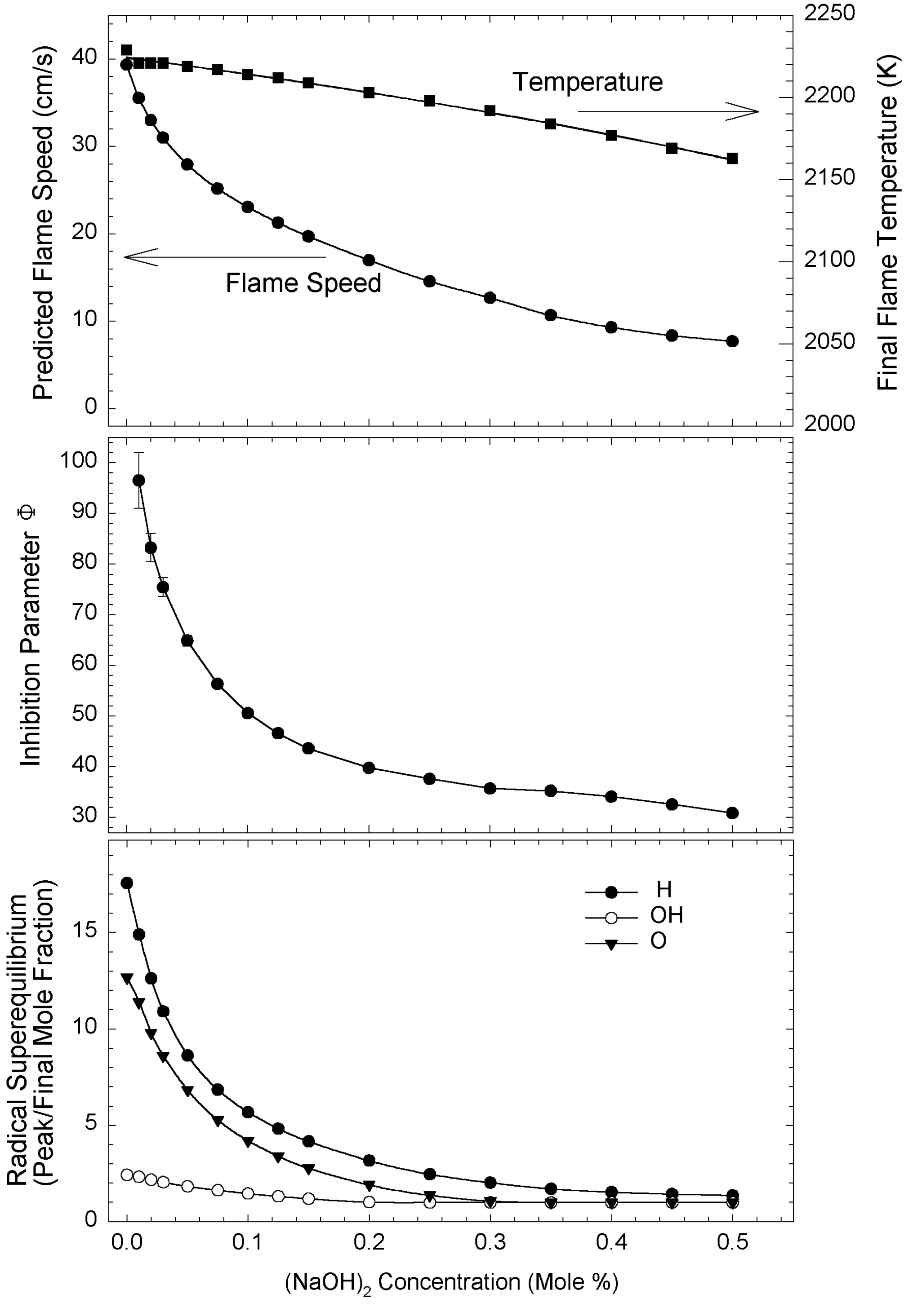

Figure 2: Flame speed, final flame temperature, inhibition parameter (defined in Ref. [3]), and superequilibrium concentrations of flame radicals computed for atmospheric pressure stoichiometric methane/air mixtures inhibited by sodium hydroxide. To simulate the evaporation process, NaOH was added to the reactants as a dimmer and required to undergo an endothermic decomposition process before inhibition chemistry could occur.

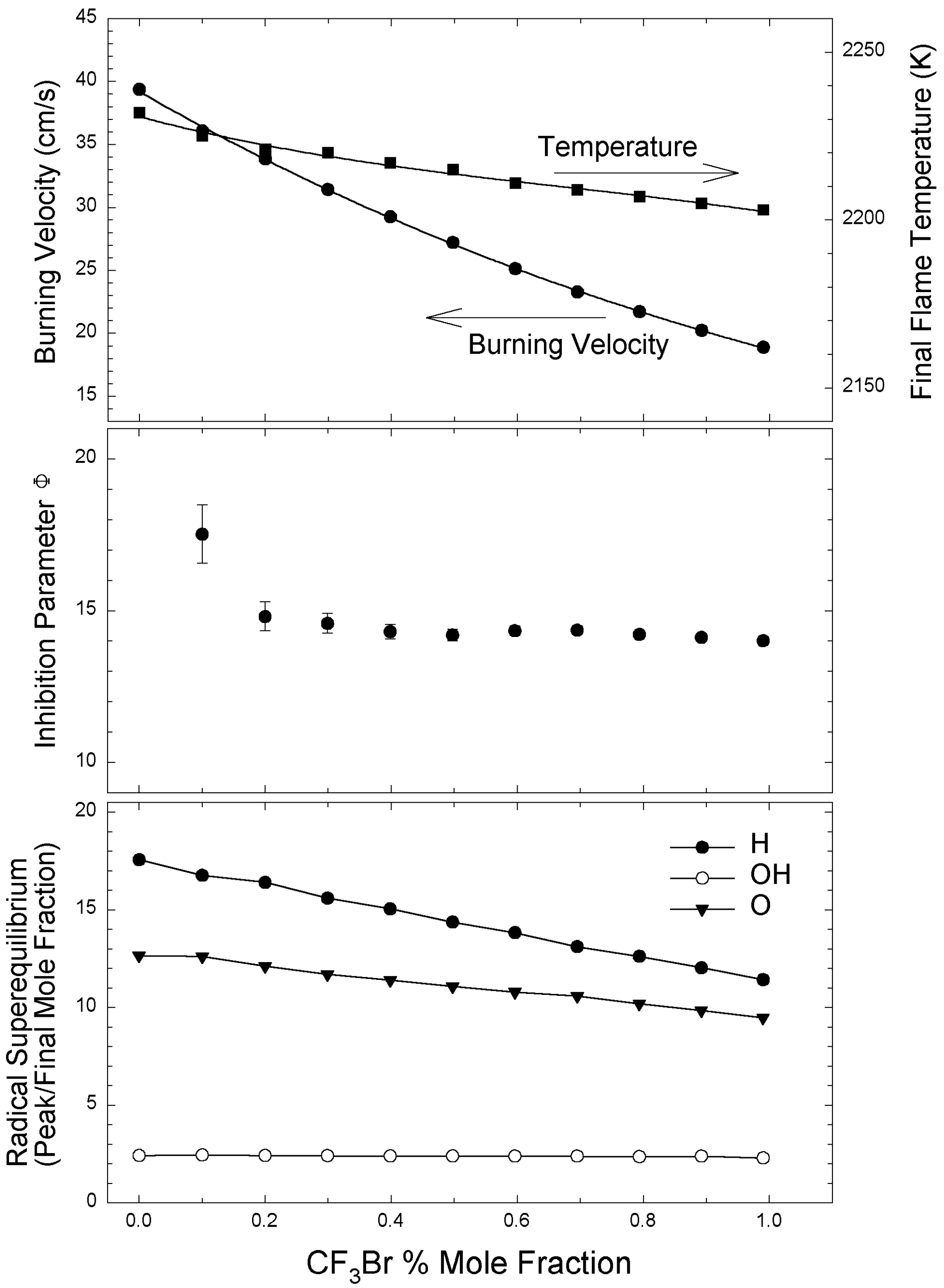

Figure 3: Flame speed, final flame temperature, inhibition parameter (defined in Ref. [3]), and superequilibrium concentrations of flame radicals computed for atmospheric pressure stoichiometric methane/air mixtures inhibited by CF_3Br.

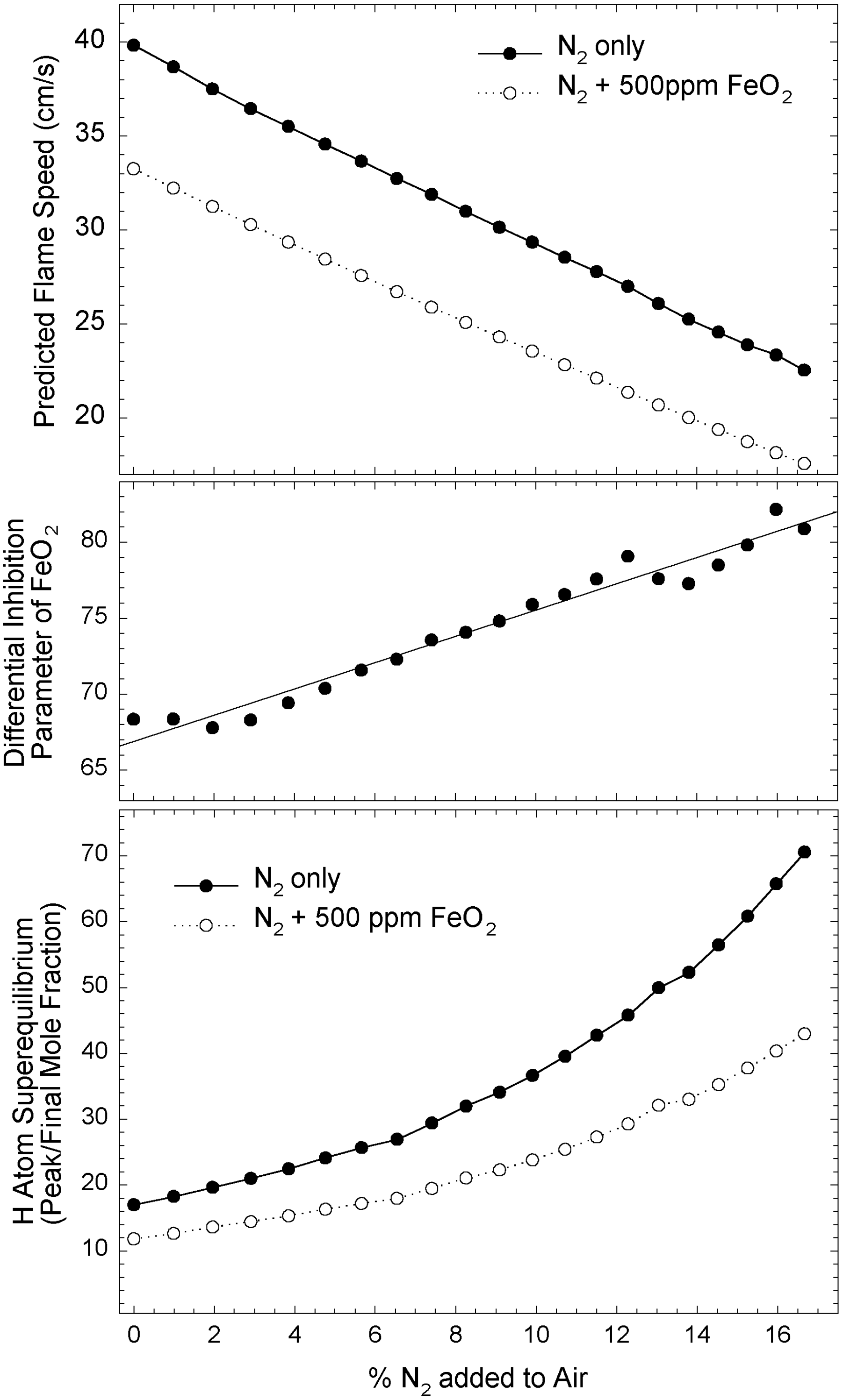

Figure 4: Flame speed, differential inhibition parameter (see text), and superequilibrium concentrations of atomic hydrogen computed for atmospheric pressure stoichiometric methane/air mixtures inhibited by nitrogen and FeO_2 in combination.

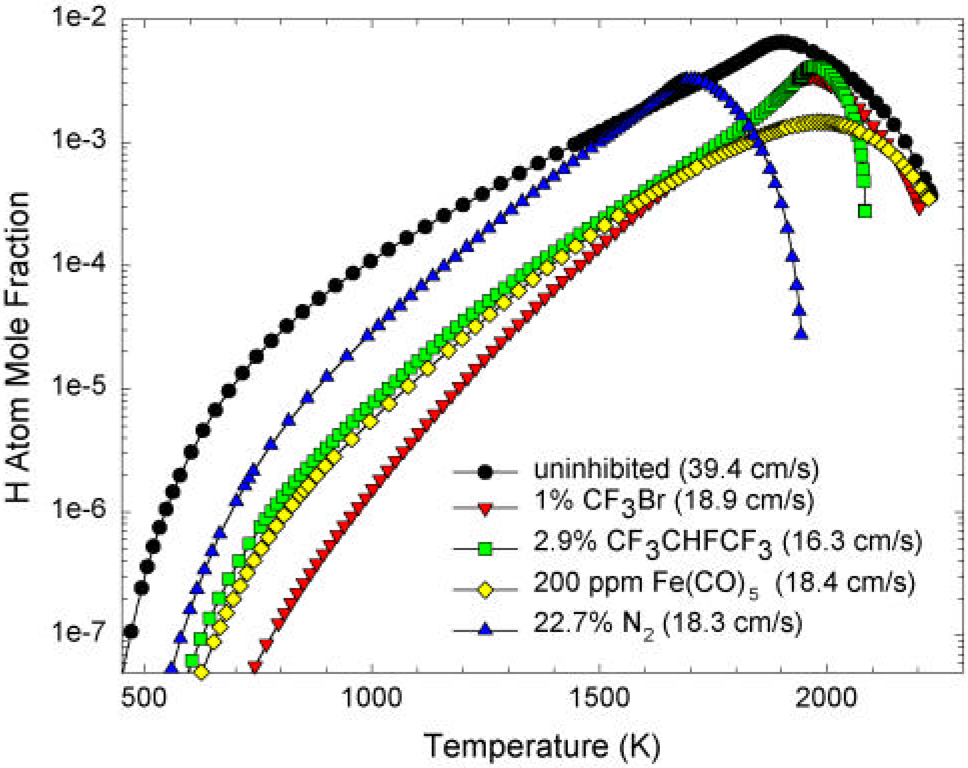

Figure 5: Mole fraction of atomic hydrogen as a function of local flame temperature for an uninhibited atmospheric pressure methane/air flame, and the same flame inhibited by various classes of suppression agents.