Chemical Limits to Flame Inhibition

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This paper deals with the ultimate limits of chemical contributions to flame inhibition. Particular attention is focussed on the inhibition cycles which regenerate the inhibitor. This leads to the definition of an idealized "perfect" inhibition cycle. It is demonstrated that for such an inhibitor in a stoichiometric methane/air flame, additive levels in the 0.001–0.01 mole percent range will lead to a decrease in flame velocity of approximately 30%. This efficiency corresponds roughly to the observed behavior of metallic inhibitors such as iron pentacarbonyl which is known to be as much as 2 orders of magnitude more effective than currently used suppressants. This correspondence between the behavior of a "perfect inhibitor" and iron carbonyl leads to the conclusion that only gas-phase processes can account for its inhibitive power. © 1998 by The Combustion Institute

INTRODUCTION

The action of chemical inhibitors on combustion has been a subject of continuing interest not only from a practical point of view but also in terms of the understanding of fundamental chemical and physical processes that are of importance. Research in this area has received a major impetus from the need to seek replacements for currently used fire inhibitors in view of their effects on the ozone layer and resulting international conventions [1].

Decreases in burning velocities of premixed flames in the presence of inhibitors are generally considered a measure of the effectiveness of a flame retardant. In the present analysis concern is with relative flame velocities. Thus problems intrinsic to the calculation of flame velocities are not of concern here. It has been known for some time and confirmed recently [2–4] that iron carbonyl, $Fe(CO)_5$ in 0.01 mole percent range, has the same effect on flame speeds of premixed methane-air flame as conventional retardants such as Halon 1301[1] (CF_3Br), in the percent level. Indeed, as can be seen in Table 1, depending on the additive, the amount necessary for a constant reduction in the velocity of a methane-air flame shows enormous variations. Thus, on a mole basis, the ratio of concentrations of CO_2, CF_3Br, and $Fe(CO)_5$ required for equal decreases in flame velocities at the levels given in Table 1 is 8.3:1:0.017. The compound CF_3Br (Halon 1301) is the commonly used retardant whose production is being prohibited in developed nations by international convention. The effect of carbon dioxide is entirely due to physical effects. It can be seen that the inhibitor efficiency of different chemical substances may differ by 3 orders of magnitude on a mole basis. For the commonly used halogenated compounds, the difference in the efficiency from purely inert diluents is about 1 order of magnitude. Another compound, chromyl chloride, appears to be in the same class as the iron carbonyl; or 2 orders of magnitude more effective than the halons (CF_3Br, $C_2F_4Br_2$) in inhibiting hydrocarbon flames [2]. For these "super" inhibitors, the extreme effectiveness can only arise from chemical effects. Other transition metal compounds also appear to be highly effective inhibitors. Finally, it was also found that metals such as Mg, Cr, Mn, Sn, and U have tremendous catalytic effect on free radical recombination in the combustion product stream. For these compounds, concentration levels in the ppm (parts per million of a mole basis) range have been found to be effective recombination catalysts [7] in the burnt gases of $H_2/O_2/N_2$ flames.

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[1] Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology that the material or equipment is necessarily the best available for the purpose.

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TABLE 1

Additive Quantity Required for 10% Reduction of Burning Velocity of Stoichiometric Methane-Air Mixture (Based on Data Presented in [2, 5, 6])

Additive	Molecules of inhibitor required per 100 molecules of CH_4 for 10% reduction of S_u	Coefficient of efficiency relative to CF_3Br
CO_2	10	0.12
CH_3Cl	4.9	0.24
Cl_2	3.8	0.32
CHF_3	3	0.4
HBr	1.8	0.67
CH_3I	1.7	0.71
CH_3Br	1.6	0.75
CF_3Br	1.2	1
Br_2	0.83	1.4
$(CH_3)_3PO_4$	0.3	4
$TiCl_3$	0.22	5.5
PCl_3	0.175	6.9
$NaHCO_3$	0.1	12
$Pb(C_2H_5)_4$	0.022	55
$Fe(CO)_5$	0.02	60

The original impetus for this paper was to develop a better understanding of the mechanism of flame inhibition by iron carbonyl. In the course of this work, it became apparent that with iron carbonyl one may be approaching the natural limit to the amount of inhibition that can be caused by chemical effects. The present discussion will therefore be presented within this framework. It is understood that this represents only one important aspect of the fire suppression problem. Extinguishment also depends on a variety of physical (heat losses, for example) and chemical processes. Other phenomena of importance are suppression and the prevention of ignition. All of these phenomena are to some degree interrelated. This is the reason for the synergisms that are often discussed in the literature. As will be seen below, in the present case relative contributions to extinguishment are effected by the loadings of the extinguishing agent.

This paper will be mainly concerned with inhibition in a premixed stoichiometric CH_4/air combustion system. We will begin with a brief survey of inhibition mechanisms. This will include a general discussion of the catalytic cycles and the individual reactions that lead to the removal of chain carriers and the ending of the combustion process. It leads naturally into an estimation of the maximum possible chemical effect on flame inhibition. Comparison will then be made with experimental data on flame inhibition and deductions will be made on the extent of departures from perfect behavior. We will then place these results in the context of the data of iron carbonyl and account for the differences in behavior of the metallic and brominated organic compounds.

Additionally, the modeling process can also be used to answer more general questions regarding the sensitivity of the overall combustion mechanism to chemical additives. These involve promotion as well as inhibition and are due to changes in reaction pathways. There are a number of well-known examples of the extreme sensitivity of chemical systems to trace impurities. Some examples include the oxidation and combustion of carbon monoxide in the presence of hydrogen-containing impurities [8], ignition delay of methane to traces of Br- and I-containing species [9], photochemical reaction of H_2 + Cl_2 to traces of NCl_3 [10], and in a completely different context, copper ion initiated oxidation of cyclohexanol in the liquid phase [11]. Such sensitivity of chemical systems to additives provides a means of controlling reaction processes through the use of small amounts of additives and thus alter the overall direction of reaction pathways.

MECHANISMS FOR FLAME INHIBITION

Earlier studies [12, 10] have led to the conclusion that flame inhibition by halogenated compounds is a consequence of the competition of the reactions

$$H + RX \Rightarrow HX + R,$$

$$H + HX \Rightarrow H_2 + X,$$

(X = Cl, Br, or I) with the chain-branching process $H + O_2 = OH + O$. The action of the inhibitor has the consequence of destroying the active radical (H atom, in this case) in the chain process. Later, it was deduced that for inhibition of hydrogen flame by HBr, several termolecular reactions, $H + Br + M = HBr + M$ and $Br + Br + M = Br_2 + M$ (where M is an inert

third body) are also important for termination and the consequent reduction of chain carrier concentration [13]. The recombination processes lead to additional formation of HBr and Br_2 and hence the regeneration of the scavenging agent. Thus HBr is a homogeneous catalyst for the recombination of H atoms. Chemical effects on flame inhibition arises from the lowering of the concentration of reactive radicals through scavenging reactions with the retardant. Inherent in this picture is not only the reaction of the radical with the scavenging species but also the regeneration of the latter, so that there is an amplifying effect in the sense of each retardant being able to neutralize more than one reactive radical [13, 14]. Thus effective inhibition mechanisms contains two important types of reactions: reactions scavenging chain carriers and processes regenerating the inhibiting agent.

Generalizing from this insight, a variety of analogous processes have been invoked to cover the action of chemicals such as Br, NO, SO_2, etc. and the postulation of a variety of catalytical cycles leading to recombination of hydrogen atoms. The simple Br mechanism of hydrogen atom scavenging consists of the following sequence of reactions [13, 15]:

$$H + HBr = H_2 + Br,$$
$$H + Br_2 = HBr + Br,$$
$$\underline{Br + Br + M = Br_2 + M,}$$
$$H + H = H_2.$$

Similarly, the NO [16] and SO_2 cycles are

$$H + NO + M = HNO + M,$$
$$\underline{H + HNO = H_2 + NO,}$$
$$H + H = H_2,$$

$$H + SO_2 + M = HSO_2 + M,$$
$$\underline{H + HSO_2 = H_2 + SO_2.}$$
$$H + H = H_2$$

The sensitivity of the ignition delay in methane/air mixtures to traces of iodine containing compounds at the ppm level of additive concentration [9] [methane oxidation, 1 atm (101 kPa), initial temperature 900–1000 K], has been attributed to the following cycle of reactions:

$$H + HI = H_2 + I,$$
$$CH_3 + HI = CH_4 + I,$$
$$I + HO_2 = HI + O_2,$$
$$I + CH_3 + M = CH_3I + M,$$
$$H + CH_3I = CH_3 + HI.$$

In this case a key role is played by the disproportionation reaction of HO_2 radical.

These mechanisms illustrate the type of reactions that are needed for inhibition. As mentioned above, these involve the removal of the reactive species and the regeneration of the scavenging agent. The necessity of the regeneration process is illustrated by the relative ineffectiveness of fluorinated compounds such as CHF_3, C_2F_6, and C_2HF_5 as flame inhibitors. Although the fluorine in these compounds can readily remove H-atoms through HF formation, the scavenging agents are not regenerated [17, 18]. Thus purely fluorinated compounds are much less inhibitive than the compounds containing bromine, with the regeneration reactions as outlined above.

Scavenging and regeneration reactions can be placed in a number of different categories. An important consequence of the present work is the confirmation that flame inhibition is much more sensitive to the latter. Thus in the case of brominated compound, the actual inhibition agent, HBr, reacts with H-atoms via a chain propagation step or,

$$H + HBr = Br + H_2.$$

In this case, the radical pool [19] is not effected by the presence of the additive. However, the reactive chain carriers (H atom) are replaced by relatively inactive Br atoms. Note that the scavenging agent can be the retardant itself, or stable and unstable breakdown products.

Regeneration reactions can take the form of chain propagating or termination processes. Some typical regeneration reactions in bromine systems, which are chain propagating [18], include

$$Br + C_2H_6 = HBr + C_2H_5,$$
$$Br + CH_2O = HCO + HBr.$$

Recombination reactions, such as

$$H + Br + M = HBr + M,$$

$$CH_3 + I + M = CH_3I + M,$$

can recreate the inhibitive species and since they are termination processes they further reduce the concentration of the radical pool. Another type of effective termination process that also leads to regeneration of inhibiting compounds is the disproportionation reaction. Some examples include

$$I + HO_2 = HI + O_2,$$

$$Br + HCO = HBr + CO,$$

and are bimolecular under all conditions. If both reactions (scavenging and regeneration) are termination steps for chain carriers, this inhibition cycle would be expected to be extremely effective.

Generalizing from the above, we can write the simplest mechanism for inhibition in terms of the following two reactions:

$$X + Inh\ (+M) = InhX\ (+M),$$

$$X + InhX = X_2 + Inh,$$

where X is the major chain carrier and Inh is the inhibiting species. Further simplification can be brought about by noting that at atmospheric pressure termolecular rate constants are usually considerably slower than the bimolecular processes. Therefore the more effective cycle will be one with bimolecular scavenging of chain carrier or X + Inh = InhX where the activation energy for the reverse process is sufficiently high or the molecule (InhX) sufficiently large so that the reaction is at the high pressure limit. Alternatively, the same results can be achieved if the overall process is that of disproportionation. In addition, it is important that the inhibitor species be inactive with respect to reactants, stable intermediates, and final products. This condition ensures the non-involvement of the inhibiting species in the overall decomposition mechanisms (except for the inhibition reactions) and maximizes its concentration. If one now assigns collisional rate constants for the remaining processes in the overall sequence of inhibition reactions (radical scavenging and regeneration), then obviously any decrease in the calculated flame velocity will be the maximum achievable.

KINETIC MODEL AND CALCULATIONAL PROCEDURES

The Premix code of the CHEMKIN(*) Library was used in the present calculations [20]. The kinetic model of C_1-C_2 oxidation was the same as in an earlier paper [18]. The boundary conditions in the calculation correspond to an adiabatic freely-propagating flame. The inhibitor efficiency was studied by modeling of its influence on the laminar burning velocity of premixed methane/air and hydrogen/air mixtures.

For the present application we add into the data base the specific reactions, which are believed to lead to inhibition. These are given below. The reader who is familiar with Chemkin should have no problems in reproducing the results. The rationale for the approach is outlined earlier. The following cases are considered:

Ideal ("Perfect") Inhibition Cycle

H-atoms are scavenged by reaction with the inhibitor (Inh) in termination processes and regenerated by reaction with H, OH, and O. The reactions are

$$H + Inh => InhH,$$

$$H + InhH => Inh + H_2,$$

$$OH + InhH => H_2O + Inh,$$

$$O + InhH => Inh + OH.$$

For simplicity we assume that the rate constants are equal and they were varied from 10^{13}–5×10^{14} $cm^3\ mol^{-1}\ s^{-1}$. An interesting issue is the consequences if these reactions are reversible. This is of course dependent on the thermochemistry. In the case of the iron carbonyl system, calculations were carried out with reversible reactions and they did not effect the results.

Model With Inhibitor Intermediate

It has been suggested [21] that in certain cases the actual inhibitor may be the result of an interaction between a particular molecule or atom with a component that is present in large

excess in the combustion zone. These may be water or CO. Such a mechanism leads to an increase in the effectiveness of those cycles where ter-molecular processes may be important. The consequence is that the initial scavenging step is replaced by two reactions

$$\mathrm{Inh} + \mathrm{CO}\ (\mathrm{H_2O}) + \mathrm{M} = \mathrm{InhCO}\ (\mathrm{InhH_2O}) + \mathrm{M},$$

$$\mathrm{H} + \mathrm{InhCO}\ (\mathrm{InhH_2O}) = \mathrm{Inh\text{-}H} + \mathrm{CO}\ (\mathrm{H_2O}).$$

The values of rate constants are 10^{16} cm^6 mol^{-2} s^{-1} and 10^{14} cm^3 mol^{-1} s^{-1}, respectively. Numerical calculations are performed with formation of $\mathrm{InhH_2O}$ and InhCO intermediates.

Iron Pentacarbonyl Inhibition

As a first approximation, the model suggested by Jensen and Jones [22] is used with the addition of two extra reactions: overall reaction of decomposition of iron pentacarbonyl and the interaction of Fe atom with molecule of oxygen with rate constants as given below:

$$k(\mathrm{Fe(CO)_5} => \mathrm{Fe} + 5\mathrm{CO}) = 6.3 \times 10^{15} \exp(-20{,}000/T)\ \mathrm{s}^{-1}\ [23],$$

$$k(\mathrm{Fe} + \mathrm{O_2} = \mathrm{FeO} + \mathrm{O}) = 1.2 \times 10^{14} \exp(-10{,}000/T)\mathrm{cm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}\ [24].$$

Then we add to the data base the set of reactions suggested in the work of Jensen and Jones [22]. These include

$$\mathrm{FeO} + \mathrm{H_2O} = \mathrm{Fe(OH)_2},$$

$$\mathrm{Fe} + \mathrm{H_2O} = \mathrm{FeOH} + \mathrm{H},$$

$$\mathrm{Fe(OH)_2} + \mathrm{H} = \mathrm{FeOH} + \mathrm{H_2O},$$

$$\mathrm{FeOH} + \mathrm{H} = \mathrm{FeO} + \mathrm{H_2}.$$

H-Atom Recombination Model

The inhibitor species directly catalyses the recombination of hydrogen-atoms through a ter-molecular process. The overall rate constant obtained experimentally by Bulewicz and Padley [7] with Cr atom as third body is used (1.5×10^{21} cm^6/mol^{-2} s^{-1}, an extraordinarily large rate constant) and is assumed to be independent of temperature.

TABLE 2

Inhibitor Concentration Required for 30 and 50% Decreasing of Burning Velocity for Different Models and Experimental Data[a]

Model and experimental data	Parameter	Inhibitor, mole percent 30%	50%
Perfect inhibitor model	5×10^{13}	0.01	0.02
	10^{14}	0.005	0.011
	2×10^{14}	0.0030	0.006
Inhibitor-reaction intermediate	InhCO	0.27	0.350
	$\mathrm{InhH_2O}$ (10^{16}, 10^{14})	0.07	0.100
$\mathrm{Fe(CO)_5}$ model		0.04	0.08
Overall rate of H recombination		0.02	0.075
$\mathrm{CF_3Br}$ model		0.50	1.0
NO cycle		6.0	>6.0
Experiment, [26] $\mathrm{Fe(CO)_5}$ additive[b]		0.012	0.02
Experiment, [4] $\mathrm{Fe(CO)_5}$ additive[b]		0.007	0.013

[a] Stoichiometric Air/Methane Flame, 1 atm (101 kPa). Results are based on specific reactions listed in text.

[b] The data are obtained by linear extrapolation from experimental results.

$\mathrm{CF_3Br}$ Inhibition Model

This is used for comparison purposes and is derived from the work of Babushok et al. [9].

NO Catalytical Cycle for Recombination

This process is also included for comparison purposes. In order to simplify the mechanism only reactions of the H, OH, and O chain carriers with NO, HNO, and $\mathrm{NO_2}$ are considered. The rate constants used are derived from Baulch et al. [25].

RESULTS AND DISCUSSION

Table 2 contains a summary of the results of calculations on the concentrations required to achieve 30% and 50% decreases in the flame velocity. Particularly interesting is the close match between the experimental results for $\mathrm{Fe(CO)_5}$ and the perfect inhibitor model (also, Fig. 1). In contrast and in accord with experimental observations, $\mathrm{CF_3Br}$ is much less effec-

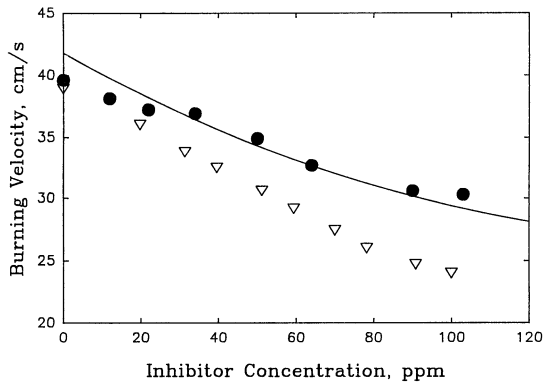

Fig. 1. Burning velocity as a function of inhibitor concentration for stoichiometric methane/air mixture at 1 atm (101 kPa). Experimental results: inhibitor, iron carbonyl solid circle [26] and inverted triangle [4]. Calculations based on perfect inhibitor model, solid line, $k = 5 \times 10^{13}$ cm^3 mol^{-1}.

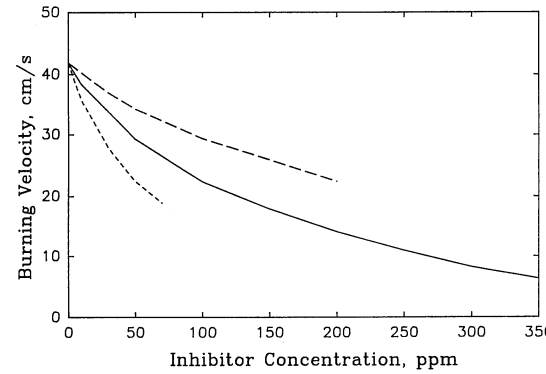

Fig. 3. Calculated dependence of burning velocity on inhibitor concentration for different rate constants in "perfect inhibitor" model. Stoichiometric air/methane flame, 1 atm (101 kPa); 5×10^{13} (long dashed line); 1×10^{14} (solid line); 2×10^{14} (short dashed line).

tive. For each inhibitor model, the burning velocity (S_u) dependence on inhibitor concentration was calculated. The following are some specific comments pertaining to each of the special cases.

Ideal ("Perfect") Inhibition Cycle

Figure 2 contains data on the dependence of burning velocity on rate constant for the perfect inhibitor model for stoichiometric methane/air flame and 0.01 mole percent of the inhibitor. The decrease in velocity with increasing rate constant is to be expected and is a demonstration of the sensitivity of this parameter to the rate constants. The comparison with data [2, 4, 26] shows that rate constants in the range of 5×10^{13}–1×10^{14} corresponds to experimental data. Figure 3 shows the dependence of burning velocity on inhibitor concentration for the different assumed rate constants. The curve is not linear and is probably related to the observed saturation effect [4] where the inhibitor becomes less effective (in terms of effect on flame velocity) as the concentration increases [18]. This decreasing influence of the additive is to a considerable extent the consequence of the "superequilibrium" concentration of chain carriers (radical overshoot) returning to near equilibrium level [27, 28]. This has the consequence of reducing the flame velocity and hence increasing the heat loss. In this sense the initial chemical action leads to a thermal effect. This is illustrative of the complex interaction between physical and chemical effects. Figure 4 contains data on the dependence of the maximum hydrogen atom concentration in the flame zone as a function of inhibitor concentration. It can be seen that initially, with an uninhibited flame, the superequilibrium ratio $[H]_{max}/[H]_{equil}$ is approximately 20 times more than the equilibrium value. The large initial concentration decrease apparently leads to the observed high effectiveness at low concentrations. However, with increasing inhibitor concentration the absolute change in velocity with amount of inhibitor decreases drastically and the mechanism for flame propagation becomes more thermal. Of course on a per unit basis the thermal contribution is not changing. The decrease in chemical

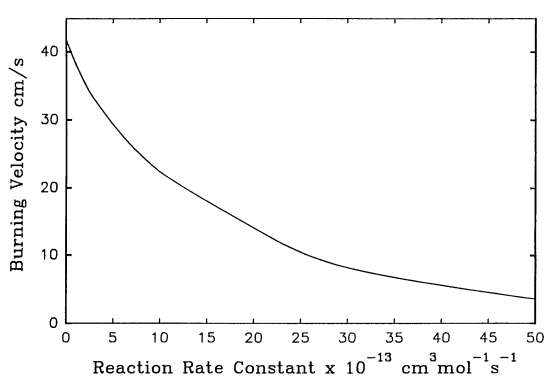

Fig. 2. Calculated dependence of burning velocity on rate constant for "perfect inhibitor." Stoichiometric air/methane flame, 1 atm (101 kPa), 0.01 mole percent additive.

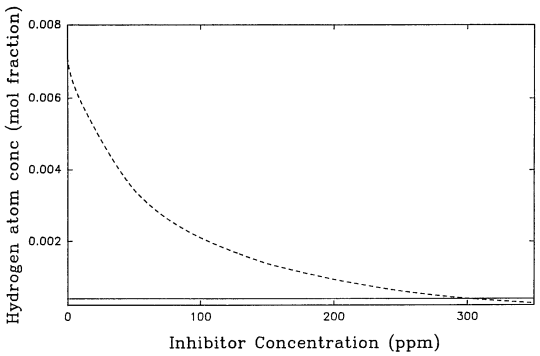

Fig. 4. Effect of "perfect inhibitor" on maximum hydrogen atom concentration in stoichiometric methane/air flame with k = 10^{14} cm^3 mol^{-1} s^{-1}. Dependence of maximum H-atom concentration on additive concentration, dashed line. Equilibrium H-atom concentration at [Inh] = 0, solid line.

contributions makes the thermal factor more important. It is tempting to relate this saturation effect to what was observed for $Fe(CO)_5$ [4]. However, the actual experimental results show a much stronger dependence. At S_u/S_{uo} = 0.5 or when the flame velocity has been reduced to one-half of the uninhibited value, the influence of the inhibitor concentration almost disappears. An alternative explanation is that the effect might be connected with vapor pressure limit of iron. The saturated vapor pressure for Fe is 0.037 mole percent at 2000 K and 1 atm (101 kPa).

The effect of adding regeneration and scavenging steps into the inhibition scheme is presented in Table 3. The key importance of regeneration reactions can be clearly seen. Particularly important are the numerical results that demonstrate the scavenging of different chain carriers do not lead to large differences in the reduction of the burning velocity. Thus the scavenging of H atoms is only 1.5 times more effective than that for O atoms in a stoichiometric CH_4/air mixture. The burning velocity reductions when only H atom is scavenged in comparison to the scavenging of all the chain carriers (H, O, and OH) are 19.5 and 23.9 cm/s, respectively. This small effect is a result of the concentrations of H, O, and OH being related by partial equilibrium relationships in the flame zone. Thus the change of the concentration of one radical leads simultaneously to changing the concentrations of other chain carriers.

TABLE 3

Influence of Scavenging Chain Carriers and Regeneration of Inhibitors on Burning Velocity

No	Models, reactions	S_u, cm/s
1	Without inhibitor	41.8
2	1 H-scavenging (H + Inh = Inh-H)	41.7
3	1 + 2 (regeneration) (H + Inh-H = H_2 + Inh)	26.5
4	1 + 2 + 3(regeneration by OH) (OH + InH = In + H_2O)	22.7
5	1 + 2 + 3 + 4(regeneration of O) (O + InH = In + OH)	22.3
6	1 + 2 + 3 + 4 + 5 (regeneration by CH_3) (CH_3 + InhH = In + CH_4)	22.0
7	1 + 3 (H atom scavenging, OH participates in regeneration)	25.0
8	1 + 4 (H atom scavenging, O participates in regeneration)	31.2
9	OH radical scavenging. Regeneration reactions H, O, OH + Inh-OH	26.0
10	O atom scavenging. Regeneration reactions H, O, OH + Inh-O	29.4
11	H, O, and OH scavenging. H, O, OH participate in regeneration	17.9

For stoichiometric hydrogen/air flames, the simulations show that inhibition effects are more pronounced. However, the modeling results show that, for the perfect inhibitor model, the decrease in flame velocity is larger than that determined experimentally. Thus, from experiments S_u/S_{uo} = 0.5 is observed at 0.3 mole percent of $Fe(CO)_5$ [26]. From modeling, the S_u/S_{uo} = 0.5 value is obtained with 0.035 mole percent.

Our calculated results show that there are negligible pressure effects with the perfect inhibitor model. This is due to the use of bimolecular processes in the model. For pressure influence to be important, there must be contributions from termolecular processes. It may well be that for some of the inhibition reactions, atmospheric pressure is sufficient to move termolecular reactions into the high pressure region.

The contribution of scavenging reactions is increased by reactions that regenerate the scavenging agent. The regeneration properties of an inhibition cycle can be characterized in terms of a value that indicates the effective number of catalytic cycles involving the inhibitor in scavenging reactions in the flame zone [29]. This number or the regeneration coefficient K_{reg} can be defined as the ratio of the total concentration

TABLE 4

Regeneration Coefficients for Stoichiometric Methane/Air Flame for Various Additives Leading to Comparable Decreases in Burning Velocities (35–50%)

Inhibitor, mole percent	Regeneration coefficient
Inh, 0.01	104
CF_3Br 1.00	7
CF_3I 1.00	3

of scavenging agent $[Inh]_{total}$ consumed (or produced) to the initial concentration of agent $[Inh]_0$ or

$$K_{reg} = [Inh]_{total}/[Inh]_0.$$

The total consumed concentration of Inh is determined by integration of the rates of reactions in which Inh is consumed until a maximum H atom concentration is achieved:

$$Inh_{total} = \int \sum W_{Inh,i}\, dt,$$

where the term $W_{Inh,i}$ is the reaction rate of the "i"th reaction consuming Inh. Table 4 contains a comparison of the calculated regeneration coefficient for the "perfect" inhibitor at the 0.01 mole percent level and that for CF_3Br and CF_3I at 1 mole percent. This demonstrates that the characteristic of the "perfect" inhibitor is its greater effectiveness in the production of regeneration cycles. Note that the effectiveness in decreasing the flame velocity, in comparison to CF_3Br, of the "perfect" inhibitor is due to the reactions of the ideal inhibition cycle being termination processes.

"Inhibitor-Reaction Intermediate" Model

This model was proposed in order to account for the scavenging of chain carriers by sodium atoms [21]. It represents a means of increasing the effectiveness of termolecular scavenging reaction by the replacement of the termolecular H + Inh + M = InhH + M process by the two step reaction sequence given above. Through the use of CO and particularly H_2O (which is usually present in much larger amounts), one expects significant increases in inhibition. This is seen to be the case in Table 2, where the presence of water has a larger effect. However

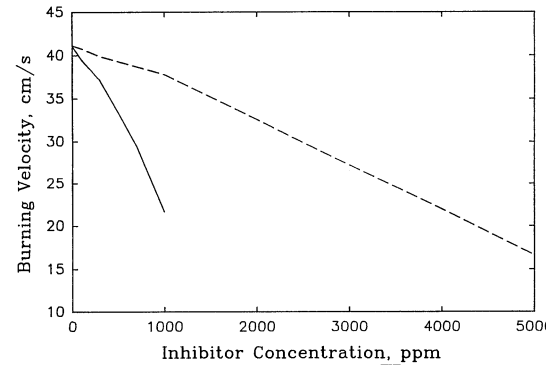

Fig. 5. Calculated dependence of burning velocity on inhibitor concentration for inhibitor-intermediate model. Stoichiometric air/methane flame, 1 atm. $InhH_2O$ (solid line), Inh-CO (dashed line). Termolecular and bimolecular rate constants of 10^{16} cm^6 mol^{-2} s^{-1} and 10^{14} cm^3 mol^{-1} s^{-1}.

this is not sufficient to account for the $Fe(CO)_5$ results. Larger termolecular rate constants of 5×10^{16} cm^6 mol^{-2} s^{-1} indicate a square root dependence of the decrease in flame velocity at low suppressant concentrations and decreasing effects as the values are increased. More important, Fig. 5 shows that the concentration dependence of the flame velocity (S_u) has an unusual character. The efficiency of inhibitor is accelerated with increasing inhibitor concentration. That is, the decrease in burning velocity increases with the inhibitor concentration. Usually, the dependence on concentration has an opposite curvature. Thus the obtained dependence is the inverse of the saturation effect [29, 30]. Such behavior probably excludes this model in many of the cases considered here.

Iron Pentacarbonyl Model

Simulation on the basis of the kinetic model discussed earlier which is based on the work of Jensen and Jones [22] leads to an underestimate of the experimental observations (Table 1). However, it is clear that a reasonable adjustment of the rate constants can bring calculated results into agreement with the experimental observations.

Overall Rate of H Atom Recombination

The use of overall rate constant of H-atom recombination on metallic atoms [7] leads to

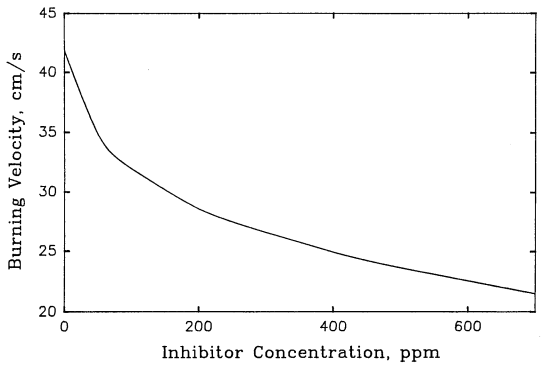

Fig. 6. Calculated dependence of burning velocity vs inhibitor concentration based on catalyzed process for H atom recombination. Stoichiometric air/methane flame, 1 atm (101 kPa).

approximately the same results as for iron pentacarbonyl $Fe(CO)_5$. It is interesting that H atom recombination leads to a faster saturation than the $Fe(CO)_5$ model due to quadratic dependence of scavenging rate on H-atom concentration (Fig. 6).

CF_3Br and NO as Inhibitors

As noted earlier, the calculations for these compounds were for purposes of comparison. All results are summarized in Table 2. It is seen that for 50% decrease in burning velocity, the CF_3Br concentration required is 50 times more than that for $Fe(CO)_5$. For NO, the situation is even worse, with 5% mole percent NO additive only a 25% decrease of burning velocity is attained.

CONCLUSION

There are a number of interesting consequences that can be derived from this study. First, there is a natural limit to the extent that ground state neutral chemistry can contribute to flame inhibition. This is hardly surprising since obviously chemistry cannot proceed faster than the collision number. Nevertheless, this has never been placed on a quantitative basis. This limit is apparently in the 0.001 to 0.01 mole percent level of additive for pronounced effect on methane combustion processes. For other fuels it may be necessary to carry out similar studies. We do not expect large changes in these numbers. The experimental results on the metal systems suggest that they are very close to this limit. Thus it is not likely that one can obtain much more efficient inhibitors. Second, it appears that flame suppression properties are much more sensitive to the nature and rate of the regeneration processes than those for scavenging.

For the metal systems considered here, it is highly unlikely that surface processes are making contributions. The concentration of particles must be even lower than that of gas phase species. Although the reaction cross sections may be larger, this will be offset by the species that are within the particles and therefore unable to scavenge reactive radicals. With increasing metallic additive concentrations condensation processes will effect the scavenging reactions. At low concentration levels it is hard to see how this can enhance the inhibition process. Thus any contributions from heterogeneous inhibition processes in methane combustion must involve loadings that are higher than that determined here.

Finally, the simulations show that the saturation effect arises very naturally from the reduction of reactive radicals to an equilibrium concentration and is probably characteristic of all inhibitors.

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