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Influence of Bond Energies on Catalytic Flame Inhibition: Implications for the Search for New Fire Suppressants

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14. ABSTRACT We have conducted computational investigations of the conditions necessary for a substance to be an efficient flame suppressant. Of particular interest is identification of additional chemical elements, which might be expected to have promising suppression properties, particularly by catalytic scavenging of flame radicals. Bromine, sodium, and iron are used as examples of prototypical H + H, H + OH, and O + O scavenging cycles, respectively. For each element, a simplified kinetic mechanism involving a single scavenging cycle was employed. The effect of hypothetical changes in bond dissociation energies on reduction of burning velocity of a premixed methane/air flame by these elements is determined. Efficient radical scavenging is possible only if a suppressant atom or radical binds to one of the primary flame radicals (H, O, or OH) with a bond energy in the range of 70-100 kcal/mole.								
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INTRODUCTION

A principal goal of fire suppression research in recent years has been the identification of environmentally benign fire suppressants having efficiency comparable to the stratospheric ozone depleting Halon 1301 (CF_3Br). The suppression effectiveness of CF_3Br and related compounds is primarily due to the chemical activity of bromine [1-3], which participates in a catalytic cycle and reduces concentrations of radical species involved in flame propagation.

Comparison of CF_3Br to agents that extinguish fires through physical effects, indicates that, with the unique exception of liquid water [4,5] suppression properties must be as good or better than Halon 1301) are likely to possess chemical suppression properties. Furthermore, high chemical suppression efficiency is most easily achieved via a catalytic cycle [6], whereby each molecule of suppressant recombines several flame radicals.

Many chemical elements besides bromine have been shown to exhibit catalytic radical scavenging in flames; several show exhibit catalytic suppression behavior much stronger than that of bromine [7], although practical issues have limited their implementation. Among the halogens, iodine as well as bromine is a good catalytic scavenger [8,9]. Among non-halogens, good suppression efficiency has been demonstrated for alkali metals [10], phosphorus [11], and several transition metals including iron [12], lead [13], chromium [14], and manganese [15]. The elements comprising this list vary greatly in their chemical properties, while other elements in the same group of the periodic table (e.g. nitrogen, fluorine) do not cause efficient catalytic suppression.

Finding a common basis for efficient chemical suppressants, whose results can be extrapolated to other elements whose combustion chemistry has not yet been thoroughly explored, is desirable. Previous work has pointed to binding energy of a suppressant to one or more flame radicals as an important parameter [16-18]. This approach has been used previously to explain, for instance, the greater suppression effectiveness of bromine compared to chlorine. [16]. The present paper broadens the scope of the previous work by focusing on a common thermodynamic basis for catalytic suppression by different *families* of elements, and different *types* of catalytic cycles. The rationale for revisiting the effect of bond energies at the present time is threefold:

1) Computational tools now exist to model the effect of thermodynamics directly, rather than resorting to simplifying approximations such as zone modeling of flame structure [17] or partial equilibrium assumptions of species concentrations [16].

2) The current research need is to assess the fire suppression potential of elements that have not yet been extensively investigated, rather than to explain the behavior of elements whose properties are already (empirically) known. By contrast, the work which elucidated the suppression kinetics of bromine was performed after halons were identified and implemented as fire suppressants.

3) A great deal of additional chemical kinetic data is now available, including provisional suppression mechanisms for a number of non-halogen species.

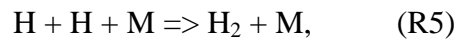
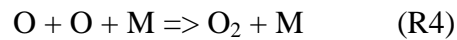
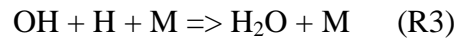
In the calculations presented here, simplified but representative catalytic cycles for known inhibitors (bromine, sodium, iron) are used in conjunction with detailed kinetic modeling of the hydrocarbon flame structure.

GENERAL FEATURES OF CATALYTIC SCAVENGING CYCLES

In most flames, the peak concentrations of the radicals H, O, and OH are much higher than the thermal equilibrium concentrations at the adiabatic flame temperature. This is a consequence of the kinetic rates of the chain branching reactions, for example

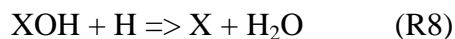
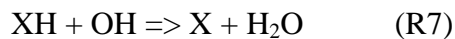


exceeding the rates of chain termination reactions such as



which require a third body for stabilization of the product [19]. Chemical fire suppressants generally participate in a catalytic cycle whose net effect is equivalent to one of the recombination reactions.

For a substance to scavenge flame radicals, there must exist some species X derived from the inhibitor which can bond to H, O, or OH. The species XR, where R is one of the flame radicals, must react with another flame radical R' to form X and RR', where RR' is usually a stable molecule such as H₂, H₂O, or O₂. Possible scavenging reactions include [20]:



To complete the cycle, X must then be converted back to XR through one or more steps. For significant inhibition to occur, the kinetic rate of the scavenging cycle must exceed that of the equivalent direct recombination reaction.

Inhibition by bromine occurs primarily through (R6) and to a lesser extent (R7) [21], while alkali metals operate primarily through (R8) [22]. Reaction (R9) is likely to occur for metallic elements [23]. Some elements, including iron [23] and phosphorus [24], are thought to participate in more than one cycle. The object of the present study is to investigate the influence of dissociation energies of the species XR on suppression behavior.

COMPUTATIONAL METHODOLOGY

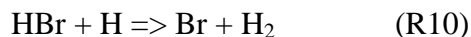
The computer code PREMIX [25] was used to model freely propagating atmospheric pressure premixed flames. The baseline condition consisted of stoichiometric methane/air, with an initial reactant temperature of 298.2 K. Tolerances for mesh refinements in PREMIX were set as follows: GRAD = 0.10, CURV = 0.20, up to a maximum of 150 grid points. Multicomponent viscosities and thermal diffusion (Soret effect) were used. The computational domain extended 25 cm from the flame into the reactants gases, and 60 cm into the exhaust gases. The domain was extended in such a way that on both boundaries, the second last grid point was 1 cm from the boundary.

The reaction set given in GRI-Mech 2.11 [26] (without nitrogen chemistry) was used for modeling the uninhibited flames. Calculations were carried out using bromine, sodium, and iron as examples of chemical inhibitors. Kinetics of chemical inhibition for these elements were added to the hydrocarbon mechanism as described below.

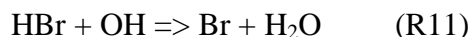
KINETIC MECHANISMS OF SPECIFIC INHIBITORS

Inhibition by Halon 1301 (CF_3Br) and the associated radical scavenging involving bromine has been the object of a number of both experimental and modeling studies. Mechanisms have recently been proposed for alkali metals, and for iron, although the current validation status of these models is more tentative than for bromine.

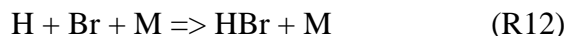
The inhibition cycle of bromine is believed to proceed by H atom scavenging [16,17]. The reaction



is thought to be the primary scavenging reaction, with the reaction with OH



also contributing. The conversion of Br to HBr involves several pathways. The direct recombination



has rather slow kinetics and is typically *not* the predominant pathway. Atomic bromine can abstract hydrogen atoms from such species as HO_2 , HCO and CH_2O ; these play an important role in most flames.

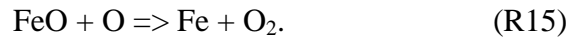
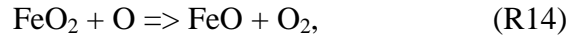
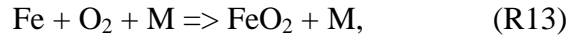
We constructed two simplified kinetic mechanisms describing inhibition by bromine. Both mechanisms include Br and HBr as the only bromine-containing species. For these calculations HBr was chosen as the bromine containing reactant. The mechanisms are listed in Table 1. In the first mechanism HBr is assumed to react only with atomic hydrogen to form Br, which is converted back to HBr by a direct recombination with H, as well as abstraction of H from HO_2 , HCO , and CH_2O . The

Table 1**Kinetic mechanisms for suppressants**

$k = AT^b \exp(-E_a/kT)$	$A(\text{cm}^3, \text{mol}, \text{s})$	b	$E_a(\text{cal/mol})$	Remark.
Mechanism for Na (H + OH cycle only-Fig. 9)				
$(\text{NaOH})_2 + \text{M} = \text{NaOH} + \text{NaOH} + \text{M}^a$	3.0E14	0.0	48000	
$\text{NaOH} + \text{H} = \text{Na} + \text{H}_2\text{O}$	1.0E13	0.0	1970	
$\text{Na} + \text{OH} + \text{M} = \text{NaOH} + \text{M}^a$	1.8E21	-1.0	0	
Mechanism for Br (reactions in common for all cycles)				
$\text{H} + \text{Br} + \text{M} = \text{HBr} + \text{M}^a$	1.92E21	-1.86	0	b
$\text{Br} + \text{CH}_2\text{O} = \text{HBr} + \text{HCO}$	1.02E13	0.0	1590	c
$\text{Br} + \text{HO}_2 = \text{HBr} + \text{O}_2$	8.43E12	0.0	1172	c
$\text{Br} + \text{HCO} = \text{HBr} + \text{CO}$	1.69E14	0.0	0	d
Addition for Br (H + H cycle-Fig. 7):				
$\text{HBr} + \text{H} = \text{H}_2 + \text{Br}$	6.25E13	0.0	2405	b
Addition for Br (H + OH cycle-Fig. 8):				
$\text{HBr} + \text{OH} = \text{H}_2\text{O} + \text{Br}$	6.62E12	0.0	0	e
Mechanism for Fe (O + O cycle-Fig. 10):				
$\text{Fe} + \text{O}_2 + \text{M} = \text{FeO}_2 + \text{M}^a$	1.57E18	0.0	4050	f
$\text{FeO}_2 + \text{O} = \text{FeO} + \text{O}_2$	1.73E13	0.0	0	estimated
$\text{FeO} + \text{O} = \text{Fe} + \text{O}_2$	1.73E13	0.0	0	g
^a Third body efficiencies: H ₂ :2 H ₂ O:6 CH ₄ :2 CO:1.5 CO ₂ :2 C ₂ H ₆ :3				
^b Baulch, D.L., Duxbury, J., Grant, S.J., and Montague, D.C., <i>J. Phys. Chem. Ref. Data</i> 10: Suppl (1981).				
^c Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Rossi, M.J., and Troe, J. <i>J. Phys. Chem. Ref. Data</i> 26:521-1011 (1997).				
^d Poulet, G., Laverdet, G., and LeBras, G., <i>J. Chem. Phys.</i> 80:1922 (1984).				
^e DeMore, W.B., Sander, S.P., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., Ravishankara, A.R., Kolb, C.E., and Molina, M.J., <i>Chemical kinetics and photochemical data for use in stratospheric modeling. Evaluation number 12</i> , JPL Publication 97-4: 1-266 (1997).				
^f Helmer, M. and Plane, J.M.C., <i>J. Chem. Soc. Faraday Trans.</i> 90:395-401 (1994).				
^g based on reverse reaction: Akhmadov, U.S., Zaslono, I.S., and Smirnov, V.N., <i>Kinet. Catal.</i> 29:251 (1988).				

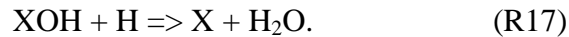
second mechanism is identical, except that HBr is allowed to react only with OH, rather than H.

The inhibition chemistry of iron has been investigated by Rumminger and Linteris [23], who identified an $\text{H} + \text{H} \Rightarrow \text{H}_2$ scavenging cycle as the most important one in hydrocarbon flames. In addition, they identified an $\text{O} + \text{O} \Rightarrow \text{O}_2$ cycle, which can be significant in moist CO flames. We use the $\text{O} + \text{O}$ cycle of iron identified by Rumminger and Linteris as an example. The cycle has three steps:



This mechanism is *not* intended as an accurate depiction of the overall inhibition chemistry of iron, only the contribution of the $\text{O} + \text{O}$ scavenging cycle. Analogous $\text{O} + \text{O}$ cycles may exist for other transition metal elements as well. In our modeling, FeO_2 is considered as the reactant. We have assumed that the kinetic rate of (R14), which has not been reported, is equal to that of (R15).

Sodium and other alkali metals, were proposed by Jensen and Jones [22] to react primarily through the cycle:



The simplified mechanism for sodium consisted of (R16) and (R17), together with a reaction converting the NaOH dimer (specified as the reactant) to the monomer to simulate an evaporation step [27]. Comparisons of thermal equilibrium calculations with NaOH(s) and $(\text{NaOH})_2$ as reactants indicate that the very minor reduction in the adiabatic

flame temperature caused by the addition of NaOH dimer is about 70% that of adding an equal amount of solid NaOH.

Using the simplified mechanism, the predicted flame speed of a stoichiometric methane/air mixture inhibited by 0.1% mole fraction of $(\text{NaOH})_2$ was 25.0 cm/s, compared to 23.1 cm/s using a more comprehensive mechanism [27] adapted from Zamansky et al. [28], and 39.4 cm/s for the uninhibited flame. This result indicates that the OH + H cycle identified by Jensen and Jones [22] is indeed the most important for suppression of near stoichiometric hydrocarbon flames.

INFLUENCE OF BOND ENERGIES ON SUPPRESSION CYCLES

For an efficient scavenging cycle to exist, the bond energy between the scavenging atom or radical X and a flame radical R must satisfy certain conditions. If it is too high, the scavenging reaction (R6)-(R9) will be endothermic. This is the case for fluorine, which binds irreversibly to hydrogen and thus cannot sustain a catalytic cycle. On the other hand, if the bond is too weak, equilibrium between XR and X + R will be so far toward dissociation that there will be insufficient XR to participate in the scavenging reactions. Stated another way, the rates of the reverse reactions should be small compared to those of the forward reactions, since any catalytic recombination cycle will become a catalytic chain branching cycle if it runs backwards.

These considerations indicate that there will be a limited range of bond energies for which an efficient scavenging cycle can exist. Putting these qualitative arguments on a quantitative basis by computational investigation of the effect of hypothetical changes in bond energies on suppression efficiencies allows the determination of the bond

energies compatible with efficient suppression. Suppression depends on kinetic as well as thermodynamic factors, so appropriate bond energies by themselves do not guarantee good suppression properties. The elements chosen here as examples, however, are known to have good suppression properties, so they possess kinetics favorable to scavenging.

Bromine was used as the example element for Reactions (R6) and (R7), sodium for (R8), and iron for (R9). All of these elements have several bond energies which may be hypothetically relevant to combustion. In order to simplify the situation so that sensitivity to bond energy can be determined in a relatively straightforward way, it was assumed that only one catalytic cycle involving one type of bond existed for each element.

For each set of calculations, the thermodynamic functions for the species XR were not altered, but heat of formation of the species X at 298K was varied, while keeping the heat capacity and entropy unchanged. This has the effect of changing the dissociation energy of X-R. In the kinetic mechanisms, the chemical reactions for the scavenging cycle were written in the exothermic direction, and the Arrhenius parameters of the forward reaction were unchanged. All reactions are assumed to be reversible, however, so changing the heat of formation alters the activation energy of the reverse reaction, even without any explicit changes to the kinetic parameters.

In the PREMIX code, the facility exists for determining the sensitivity of the solution vector, including the flame speed eigenvalue, to changes in the heats of formation of species (HSEN keyword). This is distinct from sensitivities with respect to changes in the kinetic rates (ASEN keyword) which are more commonly reported in

modeling studies. Sensitivity analysis, however, only provides the first derivative of the flame structure with respect to thermodynamic or kinetic quantities. As seen below, the dependence of suppression efficiency on heats of formation is non-monotonic. A small sensitivity coefficient for the enthalpy of a particular species on the flame speed may mean that the species in question is unimportant to suppression, or it could mean that its enthalpy is very close to the optimal value, leading to a vanishing first derivative.

Bromine: H + H and H + OH Recombination

For this series of calculations HBr was chosen as the bromine containing reactant. The kinetic mechanism was chosen to model the effect of a single catalytic mechanism, with Br and HBr as the only bromine species. Two sets of calculations were performed, the difference being whether HBr was assumed to react with H or with OH. Fig. 1 shows the predicted flame speed of a stoichiometric methane/air mixture inhibited by an 0.5% mole fraction of HBr. The catalytic cycle is most efficient for H-Br bond energies between 65 and 90 kcal/mole.

The accepted value of the H-Br bond energy lies near the upper limit of the range which permits an efficient catalytic cycle (Fig. 1). The bond energy of H-I is near the lower limit of the optimal range, while the H-Cl bond is too strong for good suppression. The bond energy of H-F (135 kcal/mole) is so high that it is completely inert in this environment. Although kinetics of the analogous reactions are somewhat different for the other halogens, the bond energy factor by itself leads to the correct prediction that iodine has a suppression effect nearly equal that of bromine [9], while chlorine has a much smaller effect [3].

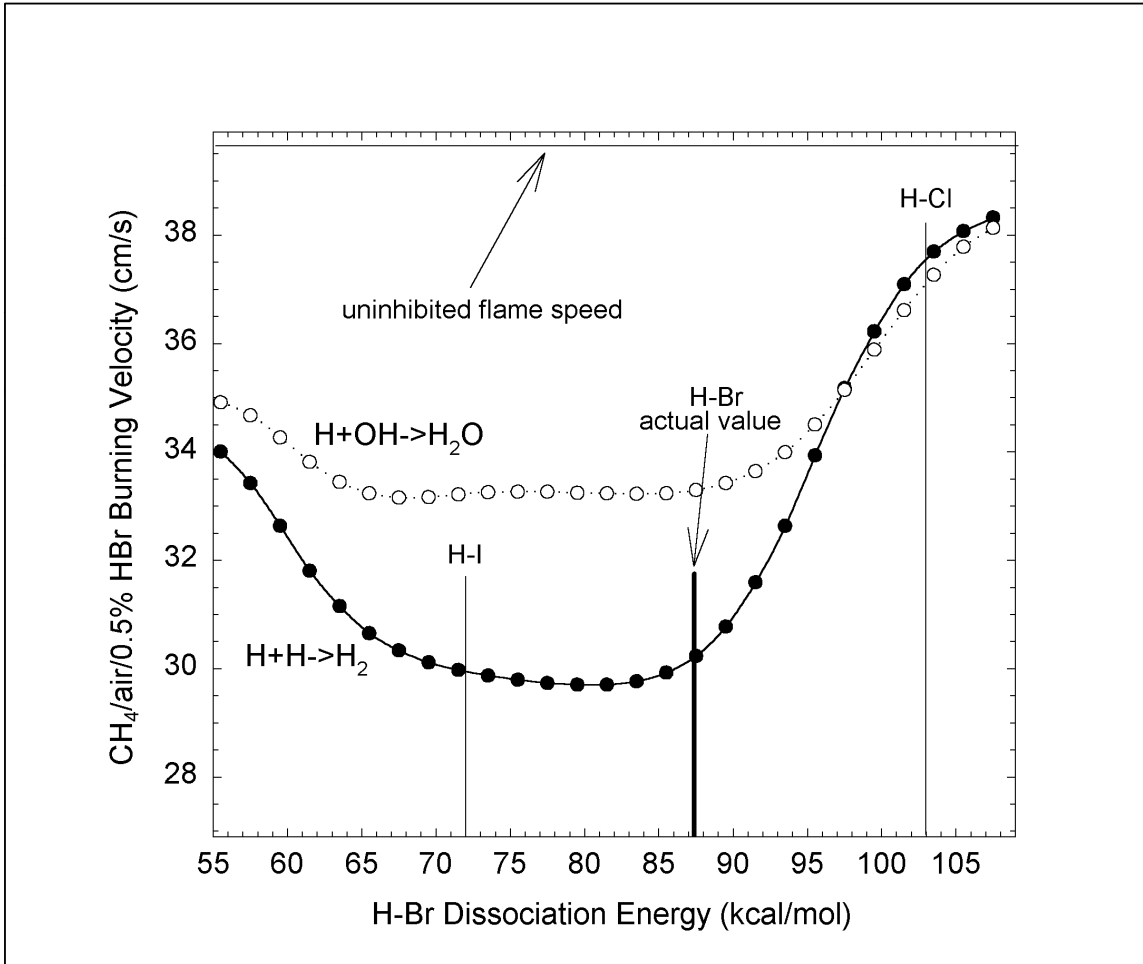


Fig. 1. Calculated flame speed as a function of H-Br bond energy (see text) for premixed methane/air flames inhibited by 0.5% HBr using the H + H and H + OH scavenging cycles of Table 1. The accepted values for the bond energies of H-Br, H-Cl, and H-I are indicated by vertical lines.

Sodium: OH + H Recombination

The effect of hypothetical variation of the Na-OH bond energy is illustrated in Fig. 2. There is a more pronounced falloff in suppression efficiency with bond energy than for either of the bromine scavenging cycles. It is seen that the Na-OH bond energy is close to the optimal value for good suppression, as are the bond energies for all the other alkali metals except lithium. Experimental studies have found that potassium is a considerably more efficient suppressant than sodium [7]. In view of the similarity of the

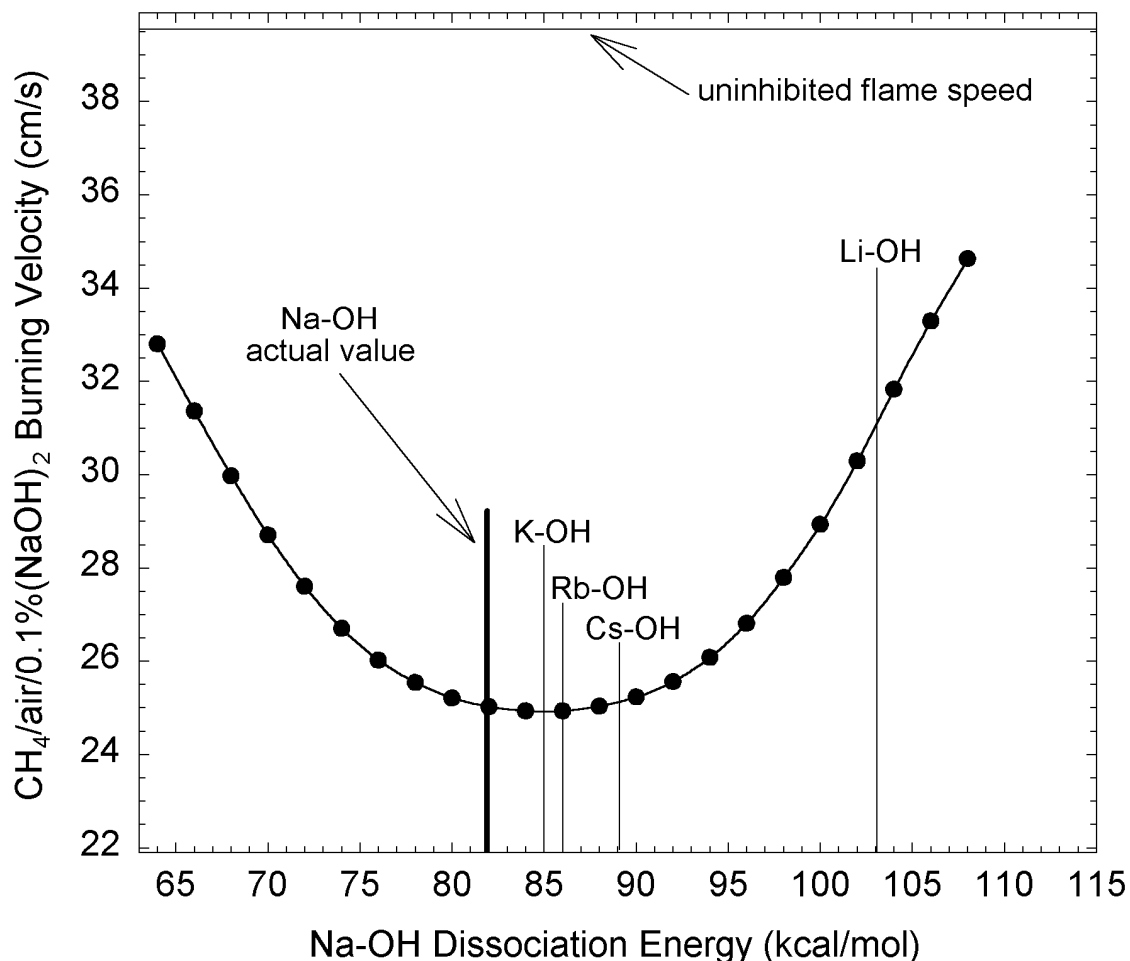


Fig. 2. Calculated flame speed as a function of Na-OH bond energy (see text) for premixed methane/air flames inhibited by 0.1% (NaOH)₂ using the H + OH scavenging cycle of Table 1. The accepted values of X-OH bond energies for the alkali metals are indicated by vertical lines.

thermodynamic properties, this difference may be due to differences in kinetic rates between the two elements, particularly for the recombination step (R16).

Iron: O + O Recombination

The three step O + O catalytic cycle modeled for iron has two relevant bond energies, Fe-O and OFe-O, which differ by about 3 kcal/mole. The bond energies were

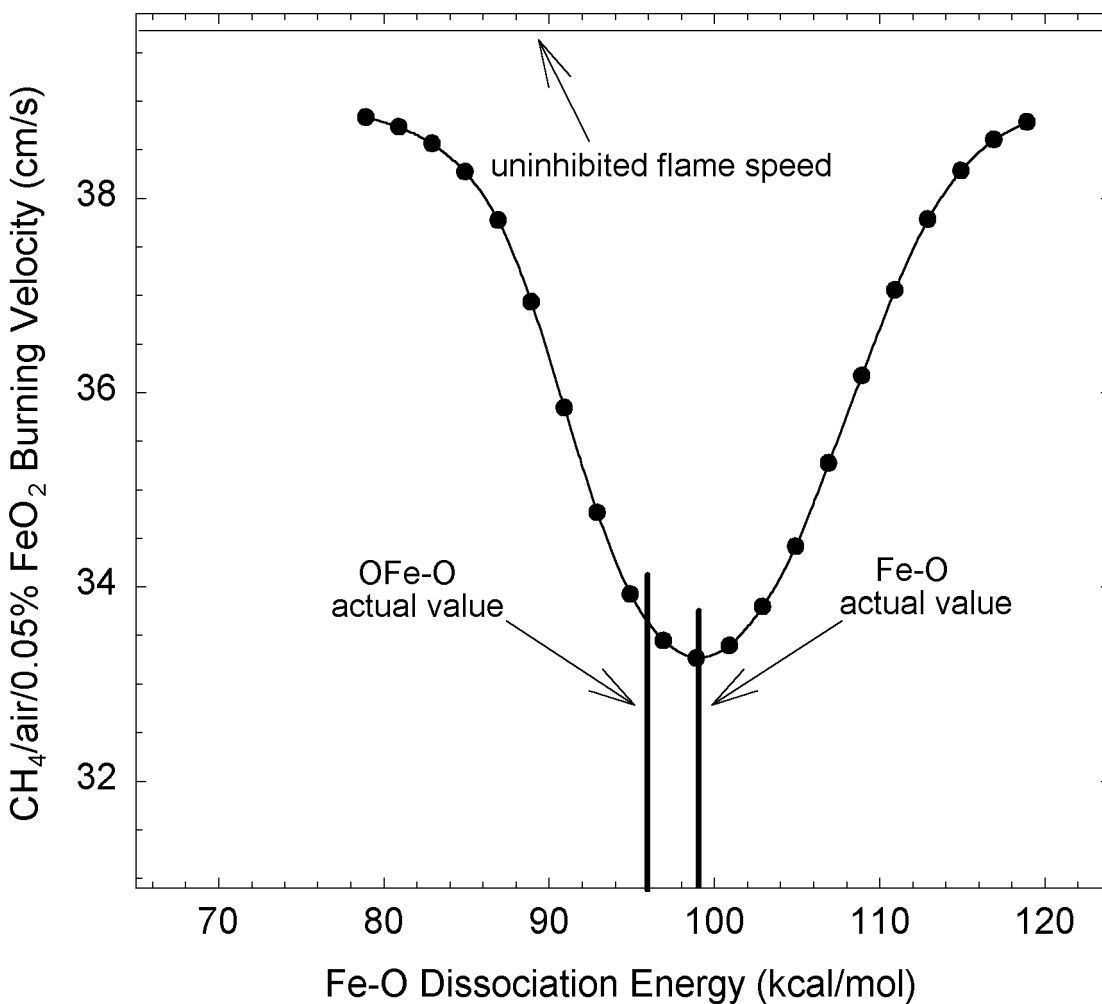


Fig. 3. Calculated flame speed as a function of Fe-O bond energy (see text) for premixed methane/air flames inhibited by 500 ppm FeO₂ using the three step O + O scavenging cycle of Table 1. The accepted values of the Fe-O and OFe-O bond energies are indicated by vertical lines.

varied in the calculation by keeping the standard state enthalpy of FeO fixed, while varying those of Fe and FeO₂ in opposite directions from their "normal" values. For FeO₂, the "normal" standard state enthalpy used was not the actual value, but was chosen such that the bond energy of OFe-O was equal to that of Fe-O, 99 kcal/mole.

In the calculation, FeO₂ was chosen as the reactant. For most iron containing compounds such as Fe(CO)₅, the parent agent is quickly converted to Fe [12], which can then combine with oxygen through (R13), making the original identity of the iron compound unimportant. Because of iron's high suppression efficiency, a smaller concentration of suppressant was used (500ppm) than for the calculations with sodium or bromine.

Results of the calculations are shown in Fig. 3. The accepted bond energies of both Fe-O (99 kcal/mol) and OFe-O (96 kcal/mol) are close to the optimal value for efficiency of the catalytic cycle.

DISCUSSION

For efficient scavenging cycles, it appears that the bond energy between a catalytic scavenger and a flame radical must lie in the range of 70-100 kcal/mol, the optimal value varying somewhat for different net recombination reactions. This range of values is consistent with the expectation that the bond must be strong enough to be thermodynamically stable at flame temperatures, but not so strong as to prevent regeneration of the active scavenging radical. In Table 2, there is a trend that the more efficient a scavenging cycle (in terms of the inhibition parameter [6]) the more sensitive it

Table 2
Efficiencies and Sensitivities to Bond Energies of Catalytic Cycles

<u>Element</u>	<u>Net Cycle</u>	<u>Inhibition</u>		<u>D_{\max}(kcal/mol)^b</u>	<u>$\frac{\Delta D}{D_{\max}}$</u>
		<u>Parameter[6]</u>	<u>ΔD(kcal/mol)^a</u>		
Br (0.5%)	H + OH	6.9	39	77	0.51
Br (0.5%)	H + H	11.5	33	77	0.43
Na (0.2%)	H + OH	46	29	85	0.34
Fe (0.05%)	O + O	66	14	99	0.14

^a range of bond energies for which the suppression index is at least 75% of its maximum value.

^b bond energy at which the maximum value of the suppression index is achieved.

is to changes in bond dissociation energies.

Other factors also play a role in suppression efficiency, although a less definitive one than does the bond energy. In most catalytic cycles, there is likely to be at least one recombination step, e.g., $\text{Na} + \text{OH} \Rightarrow \text{NaOH}$, $\text{Fe} + \text{O}_2 \Rightarrow \text{FeO}_2$. In many cases, the recombination reaction may be the rate limiting step in the catalytic cycle. Clearly this recombination step must have a faster rate than the direct radical-radical recombination for the catalyst to cause inhibition. In general, the recombination complex is more likely to be stabilized by third body colliders if it is polyatomic, rather than diatomic. Also, if the recombination reaction involves a stable, rather than a radical flame species, it is likely to proceed faster due to the higher reactant concentrations. This is the case for the $\text{Fe} + \text{O}_2$ recombination step.

Many transition metals whose compounds show good suppression properties exhibit more than one stable valence. This does not appear to be a fundamental requirement for good suppression, since alkali metals only exhibit one valence yet are good suppressants. The existence of multiple valences greatly increases the number of

possible species, increasing the likelihood that an efficient catalytic cycle may occur. Multiple valences may also facilitate recombination reactions. If the reactant and product of a recombination reaction correspond to two stable valences of the inhibitor element, then the kinetics of the reaction may be more favorable.

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REFERENCES

1. Westbrook, C. K., *Combust. Sci. Technol.* 23:191-202 (1980).
2. Westbrook, C. K., *Combust. Sci. Technol.* 34:201-225 (1983).
3. Sheinson, R. S., Penner-Hahn, J. E., and Indritz, D., *Fire Safety Journal*, 15:437-450 (1989).
4. "Inhibition of Premixed Methane-Air Flames by Water Mist," Fuss, S. P., Chen, E. F., Yang, W., Kee, R. J., Williams, B. A., and Fleming, J. W., *Proc. Combust. Inst.* 29:361-368 (2002).
5. Pitts, W. M., Yang, J. C., Huber, M. L., and Blevins, L. G., *Characterization and Identification of Super-Effective Thermal Fire Extinguishing Agents* NIST Report NISTIR 6414, National Institute of Standards and Technology, Gaithersburg, MD, 1999.
6. Noto, T., Babushok, V., Hamins, A., and Tsang, W., *Combust. Flame* 112:147-160 (1998).
7. Babushok, V. and Tsang, W., *Combust. Flame* 123:488-506 (2000).
8. Babushok, V., Tsang, W., Linteris, G. T., and Reinelt, D., *Combust. Flame* 115:551-560 (1998).
9. Babushok, V., Noto, T., Burgess, D. R. F., Hamins, A., Tsang, W., *Combust. Flame* 107:351-367 (1996).
10. Hamins, A., *Proc. Combust. Inst.* 27:2857-2864 (1998).

11. MacDonald, M. A., Jayaweera, T. M., Fisher, E. M., and Gouldin, F. C., *Combust. Flame* 116:166-176 (1999).
12. Rumminger, M. D., Reinelt, D., Babushok, V., and Linteris, G. T., *Combust. Flame* 116:207-219 (1999).
13. Vanpee, M. and Shirodkar, P. P., *Proc. Combust. Inst.* 17:787-795 (1978).
14. Bulewicz, E. M. and Padley, P. J., *Proc. R. Soc. London A* 323:377-400 (1971).
15. Linteris, G. T., Knyazev, V. D., and Babushok, V. I., "Inhibition of premixed methane flames by manganese and tin compounds," *Combust Flame* 129: 221-238 (2002).
16. Dixon-Lewis, G. and Simpson, R. J., *Proc. Combust. Inst.* 16:1111 (1976).
17. Fristrom, R. M. and Van Tiggelen, P., *Proc. Combust. Inst.* 17:773-785 (1978).
18. The Effect of Metal Salts on Premixed Hydrocarbon Air Flames, Rosser, W. A., Inami, S. H., and Wise, H., *Combust. Flame* 7:107-119 (1963).
19. Griffiths, J. F. and Barnard, J. A., *Flame and Combustion*, 3rd Edition, Blackie Academic and Professional, Glasgow, 1995, p. 33.
20. Glassman, I., *Combustion*, 2nd Edition, Academic Press, Orlando, FL, 1987, pp.145-146.
21. Casias, C. R., and McKinnon, J. T., *Proc. Combust. Inst.* 27:2731-2740 (1998).
22. Jensen, D. E. and Jones, G. A., *J. Chem. Soc. Faraday Trans. 1* 78:2843 (1982).
23. Rumminger, M. D., and Linteris, G. T., *Combust. Flame* 120:451-464 (2000).
24. Twarowski, A., *Combust. Flame* 102:41-54 (1995).
25. Kee, R.J., Grcar, J.F., Smooke, M.D., and Miller, J.A., *PREMIX: A Fortran Program for Modeling Laminar One-Dimensional Premixed Flames*, Sandia Report SAND85-8240, 1985.
26. Bowman, C. T., Hanson, R. K., Gardiner, W. C., Lissianski, V., Frenklach, M., Goldenberg, M., and Smith, G. P., *GRI-Mech 2.11 - An Optimized Detailed Chemical Reaction Mechanism for Methane Combustion and NO Formation and Reburning*, GRI Report GRI-97/0020, 1997, Gas Research Institute, Chicago.
www.ME.Berkeley.edu/gri_mech
27. Williams, B. A. and Fleming, J. W., "CF₃Br and other Suppressants: Differences in Effects on Flame Structure" *Proc. Combust. Inst.* 29:345-351 (2002).

28. Zamansky, V. M., Lissianski, V. V., Maly, P. M., Ho, L., Rusli, D., and Gardiner, Jr., W. C., *Combust. Flame* 117:821-831 (1999).