

SUPPRESSION MECHANISMS OF ALKALI METAL COMPOUNDS

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INTRODUCTION

Alkali metal compounds, particularly those of sodium and potassium, are widely used as fire suppressants. Of particular note is that small NaHCO_3 particles have been found to be 2-4 times more effective by mass than Halon 1301 in extinguishing both counterflow flames [1] and cup-burner flames [2]. Furthermore, studies in our laboratory have found that potassium bicarbonate is some 2.5 times more efficient by weight at suppression than sodium bicarbonate. The primary limitation associated with the use of alkali metal compounds is dispersal, since all known compounds have very low volatility and must be delivered to the fire either as powders or in (usually aqueous) solution.

Although powders based on alkali metals have been used for many years, their mode of effectiveness has not generally been agreed upon. Thermal effects [3], namely, the vaporization of the particles as well as radiative energy transfer out of the flame, and both homogeneous (gas phase) and heterogeneous (surface) chemistry have been postulated as mechanisms by which alkali metals suppress fires [4]. Complicating these issues is the fact that for powders, particle size and morphology have been found to affect the suppression properties significantly [1].

In addition to sodium and potassium, other alkali metals have been studied, albeit to a considerably lesser extent. The general finding is that the suppression effectiveness increases with atomic weight: potassium is more effective than sodium, which is in turn more effective than lithium [4]. This is true even on a mass basis in spite of the increasing atomic weight of the metallic element. The difference generally observed between sodium and potassium is a factor of two to three. Since the thermodynamics and chemical behavior of the alkali metals are fairly similar, such a large difference in suppression efficiency is rather surprising, and may provide clues as to how suppression occurs due to these elements.

Alkali metals show completely different behavior from both halogens and transition metals and semimetals. Halogens (particularly bromine and iodine) participate in a catalytic cycle of H atom recombination through hydride species, HX ($\text{X}=\text{Br}, \text{I}$). The transition metals (Fe, Cr, Mn) and semimetals (P, As, Sb) possess multiple oxidation states, which may facilitate catalytic cycles involving oxide and oxyhydride species. Alkali metals do not conform to either category, since they do not possess multiple valences nor form stable hydrides. For this reason, this group of elements may provide insight into what other properties a chemical element can have to be a good fire suppressant.

The present study investigates the possible suppression mechanisms for alkali metals, aims to determine possible causes for their rather high effectiveness in general, and offers explanations for the observed differences among elements. To this end a series of calculations was performed investigating the thermal effect of the addition of alkali metal compounds to flames, as well as kinetic modeling to investigate chemical reactions important for fire suppression and identify what experimental measurements would be most useful for validation of proposed kinetic mechanisms.

THERMODYNAMIC DATA

To assess the thermodynamic effect of alkali metal compounds on flames, and to perform kinetic calculations, thermodynamic data are required for all species of interest, both the additive itself and all decomposition products that might be formed in the flame. Thermodynamic data were compiled for the entire series of alkali metals (Li, Na, K, Rb, Cs) for the following species (where X represents an alkali metal atom): X, X₂, XH, XO, X₂O, XO₂, X₂O₂, XOH(gas), X₂O₂H₂(gas), XOH(liquid), XOH(solid), X₂CO₃(liquid), and X₂CO₃(solid). The solid bicarbonates were also included for Na and K. The data were collected from a variety of sources [5-7]. For some species for which published thermodynamic tables were unavailable or very uncertain, particularly the monoxides (XO) and the dioxides (XO₂), thermodynamic functions were calculated based on spectroscopic or theoretical determinations of bond dissociation energies, vibrational frequencies, and excited electronic states. The calculation assumed the harmonic oscillator approximation for the vibrational partition function, but allowed excited electronic states to have different vibrational frequencies than the ground state. From these data, polynomial fits of the form used by the Sandia CHEMKIN program were obtained. For the condensed phase species, thermodynamic functions were extrapolated above the melting or boiling point, assuming a constant heat capacity, so that equilibrium calculations would not spuriously predict the existence of condensed phases at high temperatures due to extrapolation of polynomial fits outside their domain of validity.

Thermal equilibrium calculations using the compiled thermodynamic data were performed for stoichiometric methane/air mixtures containing a 0.19% mole fraction of each of the alkali metal carbonates (X₂CO₃) in solid form. Each calculation was performed at constant enthalpy (i.e., calculating the adiabatic flame temperature) at one atmosphere pressure, and the results are summarized in Table 1. The only alkali metal containing species present in significant concentrations at equilibrium were the gas phase metal atom (X) and the gas phase hydroxide monomer (XOH). The monoxides (XO) were the next most significant alkali metal species, but never comprised more than 0.5% of the metal atoms.

Two conclusions are apparent from the thermal equilibrium calculations. First, the addition of the carbonate powder reduces the adiabatic flame temperature by only 25-30 K. The concentrations considered here are roughly 20% of those typically required to extinguish flames. Even at a molar concentration of 1% agent, the flame temperature reduction would be less than 200 K, much less than the decrease when N₂ is added at its extinction concentration. The dominant mode of suppression must then be chemical, rather than thermal. Secondly, the identity of the metallic element has hardly any effect on the flame temperature. Thus, thermal effects do not

TABLE 1. THERMAL EQUILIBRIUM TEMPERATURES AND SPECIES CONCENTRATIONS FOR A STOICHIOMETRIC METHANE/AIR MIXTURE CONTAINING 0.19% MOLE FRACTION OF $X_2CO_3(S)$, AT 1 ATMOSPHERE AND INITIAL TEMPERATURE 300 K.

Metallic Element	Adiabatic Flame Temperature (K)	Equilibrium Mole Fractions		
		X(gas)	XOH(gas)	XO(gas)
None	2231	—	—	—
Li	2204	4.78E-5	3.71E-3	4.33E-6
Na	2200	1.85E-3	1.89E-3	1.89E-5
K	2204	9.55E-4	2.80E-3	9.21E-6
Rb	2207	6.89E-4	3.06E-3	8.36E-6
Cs	2207	3.52E-4	3.40E-3	6.53E-6

account for the observed differences in suppression efficiency between elements. The primary difference between the different metals is the degree to which the hydroxide dissociates to a metal atom and an OH radical. The dissociation energy, smallest for sodium and largest for lithium, is reflected in the very low equilibrium concentration of atomic lithium compared to sodium.

CHEMICAL KINETICS

Several radical scavenging pathways have been proposed in previous studies of alkali metals in flames. The simplest, suggested by Jensen and Jones [8], involves a two-step chemical mechanism:



where M is a third body. The kinetic cycle is carried by the two major alkali metal species present in the flame. Reaction (1) is exothermic for all the alkali metals (even though in the condensed phase, alkali metals react violently with liquid water), and occurs at a substantial fraction of the collision rate. The rate of Reaction (2) is rather uncertain, particularly at high temperatures. We performed a series of preliminary calculations of the propagation speed of a stoichiometric methane/air flame inhibited by sodium and potassium hydroxide, using this two-step mechanism. The calculations demonstrated that this catalytic cycle is more than sufficient to explain the observed suppression effectiveness.

More recent studies [9,10] have indicated that the kinetic pathways of alkali metals in flames include the species XO and XO_2 as well, and that the recombination reaction with molecular oxygen



may be comparable in importance to that of Reaction (2) under certain conditions. A more comprehensive kinetic mechanism was prepared, which included these additional reactions, based on a recent publication of Zamansky et al. [11], and studied the effect of sodium on post-flame NO_x reduction strategies. A few modifications were made to the mechanism. Since NaH is predicted to be one of the more significant trace species at thermal equilibrium, we added kinetics for this species, assuming it could be formed by a sodium atom abstracting a hydrogen atom from HO₂ or HCO. The actual importance of NaH in the kinetic pathways or in influencing the flame speed turned out to be minor, however. Also, the mechanism postulated [11] that NaO₂ has a very large, temperature independent, rate coefficient for oxidation of CO:



This reaction is of relatively little importance under the conditions [11], in which there was little CO. In our calculations, however, this reaction was predicted to dominate CO oxidation to such an extent that it caused the normal CO oxidation reaction,



to run in reverse. This deficiency was addressed by adding an activation energy to the kinetic expression for the rate coefficient of Reaction (4), assumed to be identical to that for the reaction



Using this extended mechanism, the flame speed was calculated in a stoichiometric methane/air mixture at atmospheric pressure, inhibited by NaOH. The computer code for calculating flame speeds (Sandia PREMIX) does not handle condensed phase species, so NaOH was added as a reactant in the form of the gaseous dimer, Na₂O₂H₂. A kinetic rate was added for formation of the monomer with a preexponential factor approximately equal to the collision rate and an activation energy equal to the enthalpy of dimerization (49 kcal/mole). Thermal equilibrium calculations comparing the effect of adding NaOH in solid form vs. dimeric form on the adiabatic flame temperature showed that adding NaOH(dimer) reduced T_{adiabatic} about 70% as much as adding the same quantity of NaOH(solid). Thus the calculation slightly understates the thermal effect of NaOH addition. As shown below, however, flame inhibition by alkali metals is dominated by chemical, not thermal, factors.

KINETIC MODELING RESULTS FOR SODIUM

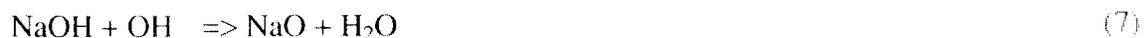
The addition of Na₂O₂H₂, using the modified kinetic mechanism [11], caused a dramatic decrease in the predicted flame speed. The top panel of Figure 1 shows the flame speed as a function of the Na₂O₂H₂ concentration. For comparison, the mole fraction of NaHCO₃ needed to extinguish a cup burner according to the study of Hamins [2] was 1-2%. Previous studies equating flame speed and extinction have assumed that flames having propagation speeds of <3-5 cm/sec will self-extinguish. Extrapolating the curve in Figure 1 and keeping in mind that

the mole fraction must be multiplied by two to equate to the number of sodium atoms in NaHCO_3 , the predicted inhibition effect is of the right magnitude.

The adiabatic flame temperature drops by only about 70 K over the range of NaOH concentrations considered in Figure 1. Even taking into account the additional enthalpy of vaporization if NaOH(solid) were the starting material, the temperature reduction would only be about 100 K, insufficient to account for the flame speed reduction. Furthermore, the strongly nonlinear shape of the flame speed curve strongly resembles the results of Babushok et al. [12] for an "ideal" chemical inhibitor, pointing to the chemical effect of the sodium. The concentrations of H, O, and OH are plotted in the bottom panel of Figure 1; chemical inhibitors generally work by reducing superequilibrium concentrations of these radicals. The calculated radical profiles reach a peak concentration in the flame front, then gradually decay to values very close to those predicted at thermal equilibrium. Therefore, the peak values of the radical profiles have been normalized by the final values at the limit of the computational domain (60 cm beyond the flame front). A concentration ratio of unity means that no radical overshoot occurs, implying that there is no more chemical inhibition to be gained by adding additional scavenging agent.

As seen in Figure 1, the H atom concentration exhibits the most overshoot in the uninhibited flame, and the OH concentration has far less overshoot than either H atom or O atom. Also plotted is the geometric mean of the normalized concentrations of the three radical species $(X_H * X_{OH} * X_O)^{1/3}$ where X denotes the normalized mole fraction. This quantity is intended as an overall measure of how much chemical inhibition can be obtained. By the time 0.5% $\text{Na}_2\text{O}_2\text{H}_2$ is added, no overshoot occurs for OH or O, and the H atom overshoot is only about 30%, compared to a factor of nearly 20 for the uninhibited flame. If the kinetics are reasonably correct, the addition of sodium compounds beyond this quantity will only produce thermal effects on the flame, since the chemical inhibition effect is nearly saturated.

Analysis of the kinetic pathways indicates that the Reactions (1) and (2) are indeed primarily responsible for flame inhibition. The recombination of $\text{Na} + \text{O}_2$ is of minor importance, and occurs primarily at low temperature, due to the relatively low dissociation energy of NaO_2 . The finding of Hynes et al. [9] that this reaction was the dominant recombination process may have been a consequence of their investigation of lean hydrogen/oxygen flames, at low temperatures and high O_2 concentrations. After Na and NaOH, the next most important species in the kinetic pathways is NaO, whose dominant reactions are



The number of sodium atoms participating in these reactions, however, is only about one-third that of Reactions (1) and (2). A simplified kinetic scheme for sodium appropriate to the conditions considered here should include at least the species Na, NaOH, and NaO, and Reactions (1), (2), (7), (8), and (9).

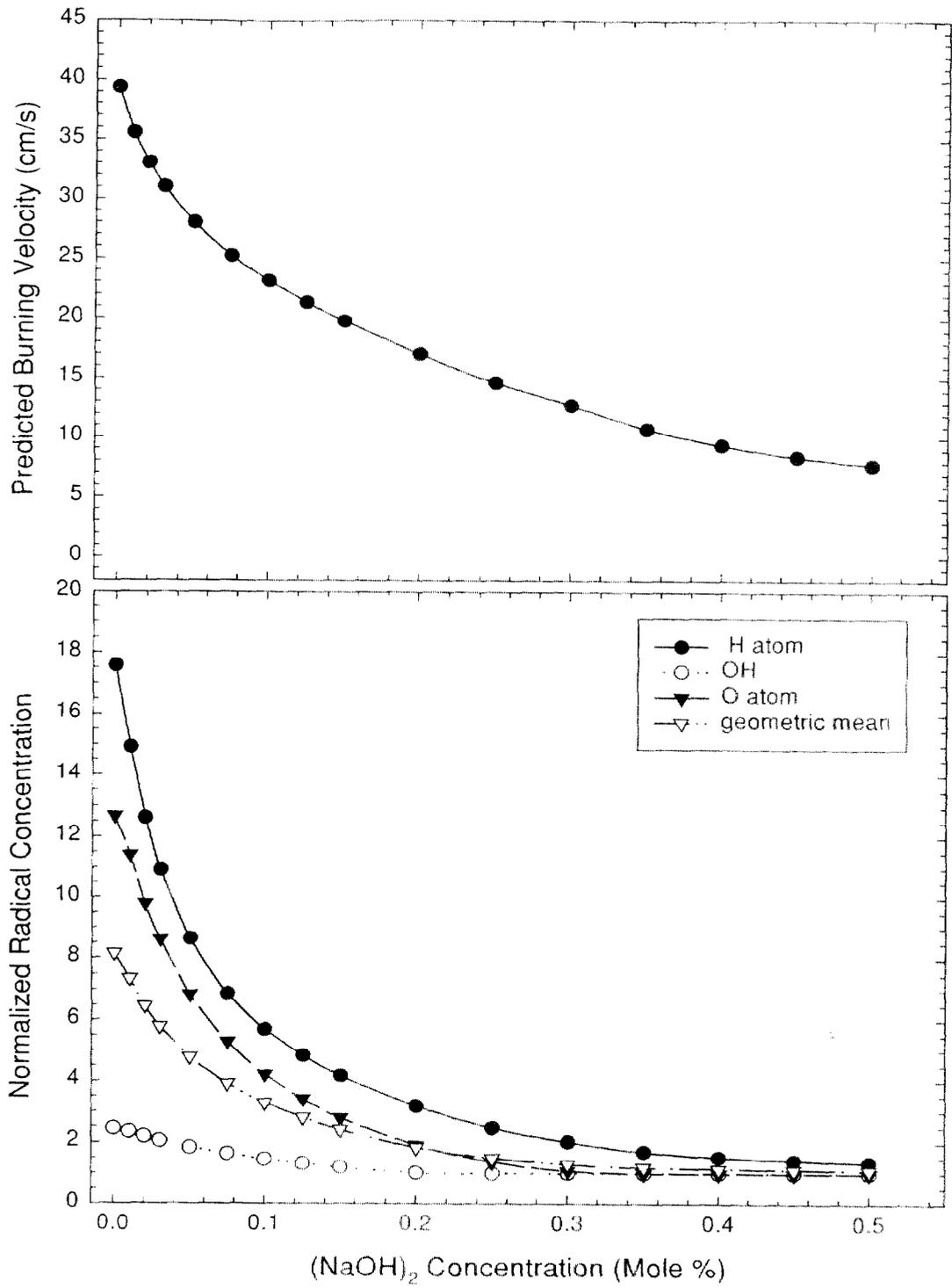


Figure 1. Predicted flame speed (top) and radical concentration overshoot (bottom) for methane/air mixtures inhibited by $\text{Na}_2\text{O}_2\text{H}_2$.

EXTENSION TO LITHIUM AND POTASSIUM

For other alkali metals, the chemical reactions relevant to suppression are even less well studied than for sodium. Nevertheless, calculations analogous to those for sodium for flames inhibited by $\text{Li}_2\text{O}_2\text{H}_2$ and $\text{K}_2\text{O}_2\text{H}_2$ were performed. As a starting point, it was assumed that the kinetic rate coefficients of the forward reactions (written in the exothermic direction in the kinetic mechanism but assumed to be reversible) are identical to the rates for the analogous sodium reactions. The one exception was that the conversion of the hydroxide dimer to monomer was given an activation energy equal to the dissociation energy for the particular element (58 kcal/mol for lithium and 45 kcal/mol for potassium, compared to 49 kcal/mol for sodium). The preexponential factor in the Arrhenius rate coefficient for this reaction was not changed between elements. Calculations were performed for a stoichiometric CH_4/air mixture containing 0.2% mole fraction of $(\text{XOH})_2$. These calculations were meant to determine how thermodynamics influences the efficiency of chemical suppression. Must sodium, potassium, and lithium have different kinetics, or can differences in their thermochemistry account for the observed trends in suppression efficiency?

The results are summarized in Table 2. For lithium, considerably less flame speed reduction occurs than for sodium, even with identical kinetics. This appears to be due to two factors. The dissociation energy of the LiOH dimer is much higher than for sodium, so the species Li and LiOH are not produced until much later in the flame, where scavenging of radicals is less effective in reducing the flame speed. Secondly, in the equilibrium calculations (Table 1), the concentration of Li is some 30 times less than for sodium, when the two elements are added in identical concentrations. The two species responsible for the catalytic cycle (Li and LiOH) are present in very unequal concentrations. In the flame calculation, LiOH is present in 10 times the concentration of Li . Since the $\text{Li} + \text{OH} + \text{M}$ reaction is likely to be the rate limiting step in the kinetic cycle, the low concentration of Li dramatically slows down the whole process. Interestingly, in the sensitivity calculations shown below, the $\text{Li} + \text{O}_2 + \text{M} \rightleftharpoons \text{LiO}_2 + \text{M}$ reaction is rather important, unlike the case for sodium. This may be a consequence of the higher dissociation energy for LiO_2 , reducing the importance of the reverse (dissociation) reaction.

TABLE 2. PREDICTED FLAME SPEEDS OF STOICHIOMETRIC METHANE/AIR MIXTURES INHIBITED BY 0.2% DIMER OF $\text{Li}_2\text{O}_2\text{H}_2$, $\text{Na}_2\text{O}_2\text{H}_2$, and $\text{K}_2\text{O}_2\text{H}_2$.

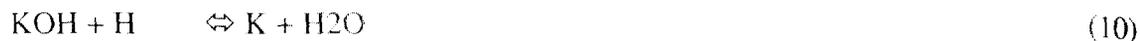
Agent	Flame speed (cm/sec)	Radical Overshoot Factor ^c
None	39.4	8.2
$\text{Li}_2\text{O}_2\text{H}_2$	30.7 ^a	7.0
$\text{Na}_2\text{O}_2\text{H}_2$	17.0	1.8
$\text{K}_2\text{O}_2\text{H}_2$	13.2 ^b	2.4

^akinetics assumed identical to sodium

^bmodified kinetic rate coefficients for $\text{KOH} + \text{H}$, $\text{K} + \text{OH} + \text{M}$, and $\text{K} + \text{O}_2 + \text{M}$

^cgeometric mean of peak H , OH , and O concentration normalized by postflame concentration

For potassium, use of the same kinetic parameters as for sodium results in the prediction of a slightly higher flame speed than for sodium, indicating less efficient suppression. The predictions are at odds with the observed behavior, indicating that differences in thermochemistry cannot be responsible for the greater suppression efficiency of potassium. To investigate what kinetic modifications would lead to better suppression for potassium, the rates for the following reactions were modified:



The rates for (10) and (12) were taken from Slack et al. [10], while that of (11) was from Husain et al. [13]. Modification of these rates did lead to the prediction of more efficient suppression by potassium, although the difference between the two elements appears to be somewhat less than that observed experimentally. Table 3 shows sensitivity coefficients of predicted flame speeds to kinetic rates of individual reactions for Li, Na, or K. One noteworthy trend is that the sensitivity coefficient of the reaction converting hydroxide dimer to monomer (necessary before any radical scavenging reactions can occur) decreases along with the enthalpy of dimerization from lithium to potassium. For lithium, breaking of the dimer is predicted to be a rate-limiting step in the inhibition process, although it is not for sodium or potassium. In Table 3, sensitivity coefficients have been normalized with respect to those of the $\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$ reaction. A negative number indicates that increasing the kinetic rate will decrease the flame speed. The larger the absolute value of the number, the more important the reaction is to inhibition.

One interesting comparison between sodium and potassium is that according to Table 2, the flame inhibited by potassium has a lower predicted flame speed than the flame inhibited by sodium, even though it has higher peak radical concentrations. This indicates that other factors must determine flame inhibition in addition to the reduction in the peak radical concentrations. Figure 2 shows profiles of temperature, major radical species (H, O, and OH), and alkali metal species for the two flames. The position of the origin on the horizontal axis is arbitrary; the positions in the two calculations are made to coincide at the point where the temperature reaches 600 K. The potassium-inhibited flame has a slower temperature rise, even though the final flame temperatures are virtually identical. The peak mole fractions of H, OH, and O are all higher in the potassium-doped flame than in the sodium-doped flame. The locations of the peaks, however, occur later, at a location where the temperature is about 100 K higher than at the location of the peaks in the sodium-inhibited flame. The concentrations of H, O, and OH early in the flame are lower in the potassium-inhibited flame. This implies that *where* the radicals are depleted is critical to inhibition, as well as *how much* depletion occurs.

TABLE 3. SENSITIVITY COEFFICIENTS OF ALKALI METAL REACTIONS FOR FLAME SPEED IN STOICHIOMETRIC METHANE/AIR MIXTURES CONTAINING 0.2% $\text{Li}_2\text{O}_2\text{H}_2$, 0.2% $\text{Na}_2\text{O}_2\text{H}_2$, OR 0.2% $\text{K}_2\text{O}_2\text{H}_2$.

Reaction	Sensitivity Coefficient
$\text{Li}_2\text{O}_2\text{H}_2 + \text{M} \rightleftharpoons 2\text{LiOH} + \text{M}$	-0.25
$\text{Li} + \text{O}_2 + \text{M} \rightleftharpoons \text{LiO}_2 + \text{M}$	-0.24
$\text{LiOH} + \text{H} \rightleftharpoons \text{Li} + \text{H}_2\text{O}$	-0.06
$\text{LiO}_2 + \text{OH} \rightleftharpoons \text{LiOH} + \text{O}_2$	-0.02
$\text{Li} + \text{OH} + \text{M} \rightleftharpoons \text{LiOH} + \text{M}$	-0.02
$\text{LiO} + \text{OH} \rightleftharpoons \text{Li} + \text{HO}_2$	0.02
$\text{NaOH} + \text{H} \rightleftharpoons \text{Na} + \text{H}_2\text{O}$	-0.32
$\text{Na} + \text{OH} + \text{M} \rightleftharpoons \text{NaOH} + \text{M}$	-0.12
$\text{Na}_2\text{O}_2\text{H}_2 + \text{M} \rightleftharpoons 2\text{NaOH} + \text{M}$	-0.11
$\text{NaO} + \text{H} \rightleftharpoons \text{Na} + \text{OH}$	-0.07
$\text{NaO} + \text{O} \rightleftharpoons \text{Na} + \text{O}_2$	-0.04
$\text{NaO} + \text{OH} \rightleftharpoons \text{Na} + \text{HO}_2$	0.03
$\text{NaO} + \text{H}_2 \rightleftharpoons \text{Na} + \text{H}_2\text{O}$	-0.01
$\text{NaO}_2 + \text{OH} \rightleftharpoons \text{NaOH} + \text{O}_2$	-0.01
$\text{NaOH} + \text{H} \rightleftharpoons \text{Na} + \text{H}_2\text{O}$	-0.32
$\text{Na} + \text{OH} + \text{M} \rightleftharpoons \text{NaOH} + \text{M}$	-0.12
$\text{Na}_2\text{O}_2\text{H}_2 + \text{M} \rightleftharpoons 2\text{NaOH} + \text{M}$	-0.11
$\text{NaO} + \text{H} \rightleftharpoons \text{Na} + \text{OH}$	-0.07
$\text{NaO} + \text{O} \rightleftharpoons \text{Na} + \text{O}_2$	-0.04
$\text{NaO} + \text{OH} \rightleftharpoons \text{Na} + \text{HO}_2$	0.03
$\text{NaO} + \text{H}_2 \rightleftharpoons \text{Na} + \text{H}_2\text{O}$	-0.01
$\text{NaO}_2 + \text{OH} \rightleftharpoons \text{NaOH} + \text{O}_2$	-0.01
$\text{KO}_2 + \text{OH} \rightleftharpoons \text{KOH} + \text{O}_2$	-0.36
$\text{K} + \text{OH} + \text{M} \rightleftharpoons \text{KOH} + \text{M}$	-0.27
$\text{KOH} + \text{H} \rightleftharpoons \text{K} + \text{H}_2\text{O}$	-0.09
$\text{K}_2\text{O}_2\text{H}_2 + \text{M} \rightleftharpoons 2\text{KOH} + \text{M}$	-0.08
$\text{KO}_2 + \text{H} \rightleftharpoons \text{KOH} + \text{O}$	-0.04
$\text{KO} + \text{O} \rightleftharpoons \text{K} + \text{O}_2$	0.02
$\text{KO}_2 + \text{H} \rightleftharpoons \text{KO} + \text{OH}$	-0.01
$\text{K} + \text{HCO} \rightleftharpoons \text{KH} + \text{CO}$	-0.01
$\text{K} + \text{O}_2 + \text{M} \rightleftharpoons \text{KO}_2 + \text{M}$	-0.01

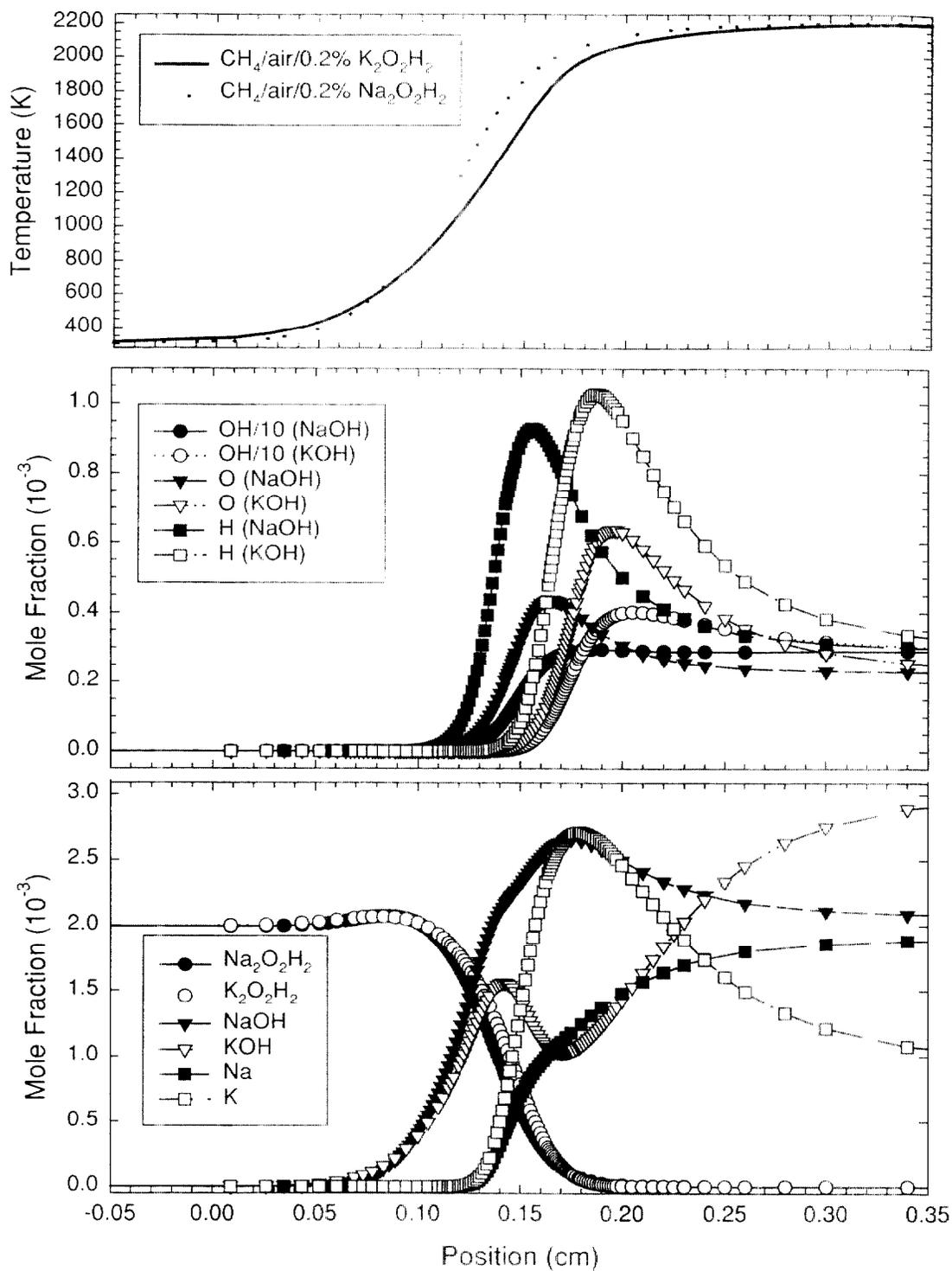


Figure 2. Predicted profiles of temperature (top), key flame radicals (middle), and alkali metal species (bottom) in methane/air flames inhibited by sodium and potassium hydroxide.

DISCUSSION

The mechanism of flame suppression by alkali metals is dominated by scavenging of the major radical species present in the flame. The lower suppression effectiveness of lithium relative to sodium can be explained by differences in thermochemistry between the two elements. This does *not* mean that the dominant effect of alkali metals on flames is thermal. Rather, it demonstrates how thermodynamic considerations can significantly influence the effectiveness of the catalytic suppression cycles. For potassium, on the other hand, the greater effectiveness relative to sodium must be due to kinetic differences. At present, kinetic parameters for the relevant reactions are not sufficiently well known to definitively conclude exactly how the kinetics must differ. One possible explanation involves the greater atomic mass and size of potassium and its probable effect on the rate of the recombination reaction $X + OH + M$. The same considerations apply to other recombination reactions such as $X + O_2 + M$, as well.

Two effects can increase the likelihood of stabilization of a collision complex by a third body. First, as the physical size of the alkali metal increases, there is a greater cross section for collision by a third body to stabilize the XOH collision complex. Secondly, as the mass increases, the collision occurs more slowly. Assuming identical potential energy surfaces, the time for a collision to occur is expected to scale as the square root of the reduced mass, μ , given by

$$\mu = M_X M_{OH} / (M_X + M_{OH})$$

where M_X and M_{OH} are the masses of the alkali metal, and the OH molecule, respectively. In the simplest approximation (treating X-OH as a two-body, one-dimensional system), the third body collision must occur within this time interval for the XOH complex to be stabilized. The product $A_m \mu^{1/2}$, where A_m is the solid angle-averaged projected area of the XOH molecule, should correlate with the likelihood of stabilization of XOH by a third body during the collision. For all the alkali metals, this product is much larger than for hydrogen (Table 4), providing a possible explanation as to why these elements enhance radical recombination. The value for potassium is roughly twice as large as for sodium, which in turn is about twice as large as for lithium.

TABLE 4. PREDICTED SIZE EFFECT ON X + OH RECOMBINATION RATES.

Element	Reduced Mass μ (amu)	Atomic Radius R (10^{-10} m)	Stabilization Cross Section $A_m \mu^{1/2}$ (relative to H)
H	0.94	0.30	1.0
Li	4.96	1.23	8.7
Na	9.78	1.54	17.7
K	11.80	2.03	31.6
Rb	14.20	2.16	38.8
Cs	15.10	2.35	46.7

Patrick and Golden [14] published a theoretical study of recombination of Li, Na, and K with OH and O₂. They predicted that potassium should have a rate 2-3 times faster than sodium with O₂, and about 30% faster than sodium with OH. Lithium was predicted to have a kinetic rate faster than sodium, but slower than potassium, for both reactions. These results are consistent with the scaling relations stated here for sodium and potassium, but not lithium. For lithium, other factors (vibrational frequencies, dissociation energy), which can influence the stabilization rate, are quite different from either sodium or potassium. In Reference 14, the authors commented that the lack of reliable experimental data, particularly on the temperature dependence of the rate, made it difficult to assess the validity of the approximations made in their derivation. If the scaling relationship in Table 4 is valid for the heavier alkali metals, differences in kinetic rates should result from physical considerations on the atomic scale, rather than differences in chemical bonding.

Previous experimental studies on the flame chemistry of alkali metals have generally monitored the metal atom, as well as the OH radical, by optical techniques. Kinetics were inferred based on changes in OH radical concentrations as the alkali metal compound was added to the flame. Unfortunately, the OH concentration is much less sensitive to the chemical suppression than either H or O concentrations. Data on either of these latter two species are likely to be more definitive in providing experimental validation for kinetic mechanisms. The observation by Slack et al. [10] that there was no discernable difference in the OH profiles between sodium or potassium addition may be a result of the low sensitivity of OH to kinetic differences.

In terms of observations applicable to flame inhibitors in general, it appears that a chemical catalytic cycle is most efficient (in a premixed flame) when the scavenging species are created early in the flame zone. In a nonpremixed flame, the condition is likely to be that the scavenger must be present at the location where the H + O₂ reaction has the largest flux, typically at a moderate temperature on the air side of the flame. A catalytic cycle for radical recombination is likely to be most efficient when all species involved in the cycle (two in the case of alkali metals) have comparable concentrations at thermal equilibrium. Finally, it appears that there may be a size effect in cases where a third-body mediated recombination reaction is needed for a catalytic cycle to exist. All other things being equal, a larger and heavier scavenging element may be more efficient, since there will be a longer time and a larger target area for a collision with a third body to stabilize the collision complex.

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REFERENCES

1. J. W. Fleming, M. D. Reed, E. J. P. Zegers, B. A. Williams, and R. S. Sheinson, "Extinction Studies of Propane/Air Counterflow Flames: The Effectiveness of Aerosols," *Proceedings*, Halon Options Technical Working Conference, Albuquerque, NM, pp. 333-342, 1998.
2. A. Hamins, "Flame Extinction by Sodium Bicarbonate Powder in a Cup Burner," *27th International Symposium on Combustion*, The Combustion Institute, 1998, pp. 2857-2864.
3. C. T. Ewing, J. T. Hughes, and H. W. Carhart, "The Extinction of Hydrocarbon Flames Based on the Heat-Absorption Processes Which Occur in Them," *Fire Mater.* 8:148-156, 1984.
4. R. E. Tapscott, E. W. Heinonen, and G. D. Brabson, "Advanced Agent Identification and Preliminary Assessment," Advanced Agent Working Group, NMERI 95/38/32350, Nov. 1996.
5. NIST Chemistry Webbook, <http://webbook.nist.gov/>
6. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. MacDonald, and A. N. Syverrud, *JANAF Thermochemical Tables, 3rd Edition*, American Chemical Society, Washington, DC, 1985.
7. HSC Chemistry Database, Ver. 3.0. Outokumpu Research Oy, Pori, Finland; <http://www.outokuntu.fi/hsc/>
8. D. E. Jensen and G. A. Jones, "Kinetics of Flame Inhibition by Sodium," *J. Chem. Soc. Faraday Trans. 1*, 78:2843, 1982.
9. A. J. Hynes, M. Steinberg, and K. Schofield, "The Chemical Kinetics and Thermodynamics of Sodium Species in Oxygen-rich Hydrogen Flames." *J. Chem. Phys.* 80:2585 (1984).
10. M. Slack, J. W. Cox, A. Grillo, R. Ryan, and O. Smith, "Potassium Kinetics in Heavily Seeded Atmospheric-Pressure Laminar Methane Flames," *Combust. Flame* 77:311-320, 1989.
11. V. M. Zamansky, V. V. Lissianski, P. M. Maly, L. Ho, D. Rusli, and W. C. Gardiner, Jr., "Reactions of Sodium Species in the Promoted SNCR Process," *Combust. Flame* 117:821-831, 1999.
12. V. Babushok, W. Tsang, G. T. Linteris, and D. Reinelt, "Chemical Limits to Flame Inhibition," *Combust. Flame* 115:551, 1998.
13. D. Husain, J. M. C. Plane, and C. C. Xiang, "Absolute 3rd-Order Rate-Constant for the Reaction Between Rb+OH+He Determined by Time-Resolved Molecular Resonance-Fluorescence Spectroscopy, OH(A²Π⁺-X²Π). Coupled With Steady Atomic Resonance-Fluorescence Measurements, Rb(6²p₁-5²s_{1/2})," *J. Chem. Soc. Faraday Trans. 2*, 81:561, 1985.
14. R. Patrick and D. M. Golden, "Termolecular Reactions of Alkali Metal Atoms with O₂ and OH," *Int. J. Chem. Kinet.*, 16:1567-1574, 1984.