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HIGH TEMPERATURE OXIDATION CHEMICAL KINETICS AND THERMODYNAMICS OF THE ALKALI METALS

FINAL TECHNICAL REPORT

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The present phase of our research to understand the high temperature oxidation chemistry of the alkali metals in flames now has been completed and has successfully explained their behavior. This basic understanding is a fundamental and initial step in resolving their nature as suppressants of gun muzzle flash and rocket afterburning. The flame chemistries of lithium, sodium and potassium now have been completely resolved and those of the two remaining alkalis, rubidium and cesium, require only final analysis but appear to follow the general observed patterns of behavior. This laser induced fluorescence study, using a matrix of about ten fuel-lean $H_2/O_2/N_2$ flames of a large variety of stoichiometries and having different flame temperatures with alkali metals of different kinetic and thermochemical properties is a particularly severe test for any analysis. Because of this, there is a significant confidence in the derived values of the dissociation energies of

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19 ABSTRACT

the MOH and MO_2 compounds. Moreover, the kinetic rate constants obtained for these high temperatures are consistent with lower temperature literature values in all cases where such data exist. Additionally, the kinetics whereby oxidation is predominantly via reactions with O_2 and H_2O, and regeneration is via reactions with flame radicals, principally OH, provides a kinetic cycle in which the alkali metal can reduce radical concentration levels. Undoubtedly, this is one, if not the principal mechanism explaining the inhibition of gun muzzle flash by these salts and merits further studies but now with larger concentrations of alkali salts.

The results of this program are to be published in a series of six or seven papers, the titles for which are listed, and which will be completed in the next several months and copies submitted to the Army Research Office.

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PROGRAM GOAL

Muzzle flash and rocket afterburning are examples of reignition phenomena which generally are undesired operationally, and are particularly so with respect to low observable characteristics. After significant trial and error testing programs over the years, it has been found that the addition of significant levels of potassium salts produce suppression but introduce significant radar scattering signatures due to the additional ionization and electron production. Obviously, in order to understand this role of potassium it is necessary to examine the detailed chemistry, which until this program was surprisingly ill-defined particularly with respect even to the nature of the species involved let alone their kinetics and thermodynamics.

Prior work on sodium[1] gave us insight into the nature of the alkali oxidation chemistries at higher temperatures and this present program has provided the means whereby not only has the work on sodium been extended and reassessed but the other alkalis lithium, potassium, rubidium and cesium have been examined for the first time. Their differing thermodynamics, ionizations and kinetics posed a demanding program which fortunately has been completely successfully providing not only the necessary kinetic and thermodynamic data but has indicated also the probable mechanism by which they can inhibit flame propagation.

EXPERIMENTAL TECHNIQUES

We are still somewhat a unique research group in invoking the combustion techniques developed by Sugden and others at Cambridge at least thirty years ago, but now with present day laser induced fluorescence methods as the major probe. The central power of the method is to study numerous flames (ten in the present program) differing in their stoichiometries and temperatures. Additionally, burned on a capillary flat reaction zone burner, these become well defined having a one-dimensional nature in which the burnt gases display non-equilibrium chemistry that decays from the reaction zone towards equilibrium. At atmospheric pressure, in hydrogen/oxygen flames, the flame radicals display a detailed balance resulting from fast kinetics which permits the basic chemistry of the flames to be well characterized. This understanding is such that additional species can be added and the resulting changes noted and used to help unravel the nature of the induced chemistry.

In the present program, laser induced fluorescence was used to measure the flame OH concentrations which in turn define the H_2O, H_2, O_2, O, OH and HO_2 concentrations. Atomic concentrations of the alkalis were monitored using saturated laser induced fluorescence. Previously, we have shown that these techniques are quantitatively accurate in these flame matrices.[1-3] Measurements are most difficult with lithium due to the too small splitting of its D-lines and a resonance mode was necessary, introducing the need for considerable efforts to minimize background scattering. In the other cases, the spectroscopy was much easier in that pumping of one line was coupled to detection of fluorescence from the other component of the $^2P_{1/2,3/2}$ doublet. However, additional problems were encountered resulting from the ionization of potassium, rubidium and cesium in the original flame matrix. In the case of potassium this could be easily resolved by suppressing the ionization with the

addition of cesium. However, in the latter cases a set of lower temperature flames had to be used to ensure that negligible ionization occurred in the 4 ms time frame. For cesium this means temperatures no higher than 1650 K.

Armed with the concentrations of the species at eight points in ten different flames this very varied data base provides a severe test for any chemical model. The additional factor of studying five alkali metals of quite different natures posed demands on the resulting explanations, but which now provide weight in supporting the level of confidence displayed by the results.

PROGRAM RESULTS

The major findings of this research are in the process of being prepared for journal publication in a series of papers the titles of which are listed later. The major results will be outlined only briefly here. The decays of potassium and lithium are illustrated in Figures 1 and 2. These show similar general patterns of behavior but whereas sodium was seen to decay overall by a factor of about 45, the corresponding decreases are 220 and 2750-fold for potassium and lithium, respectively. The chemical stabilities obviously produce very different distributions in these cases. Plotted in the form of an equilibrium constant against temperature, these data were initially used to test for equilibrations of the type

$$M + H_2O = MOH + H.$$

As seen in Figures 3 and 4, although these appear to approach this at higher temperatures and at longer times, potassium in particular displays significant deviations particularly below 2000 K. At sufficiently high temperatures the systems do approach equilibration and it was later apparent that this provides an unexpected method for checking the thermochemistry of the MOH molecules. As indicated in the figures and summarized in Table 1, although the current JANAF values for LiOH appear very accurate, those for KOH and NaOH require

Figure 1. Measured decays of atomic potassium concentration in the burnt gases of a series of oxygen rich flames.

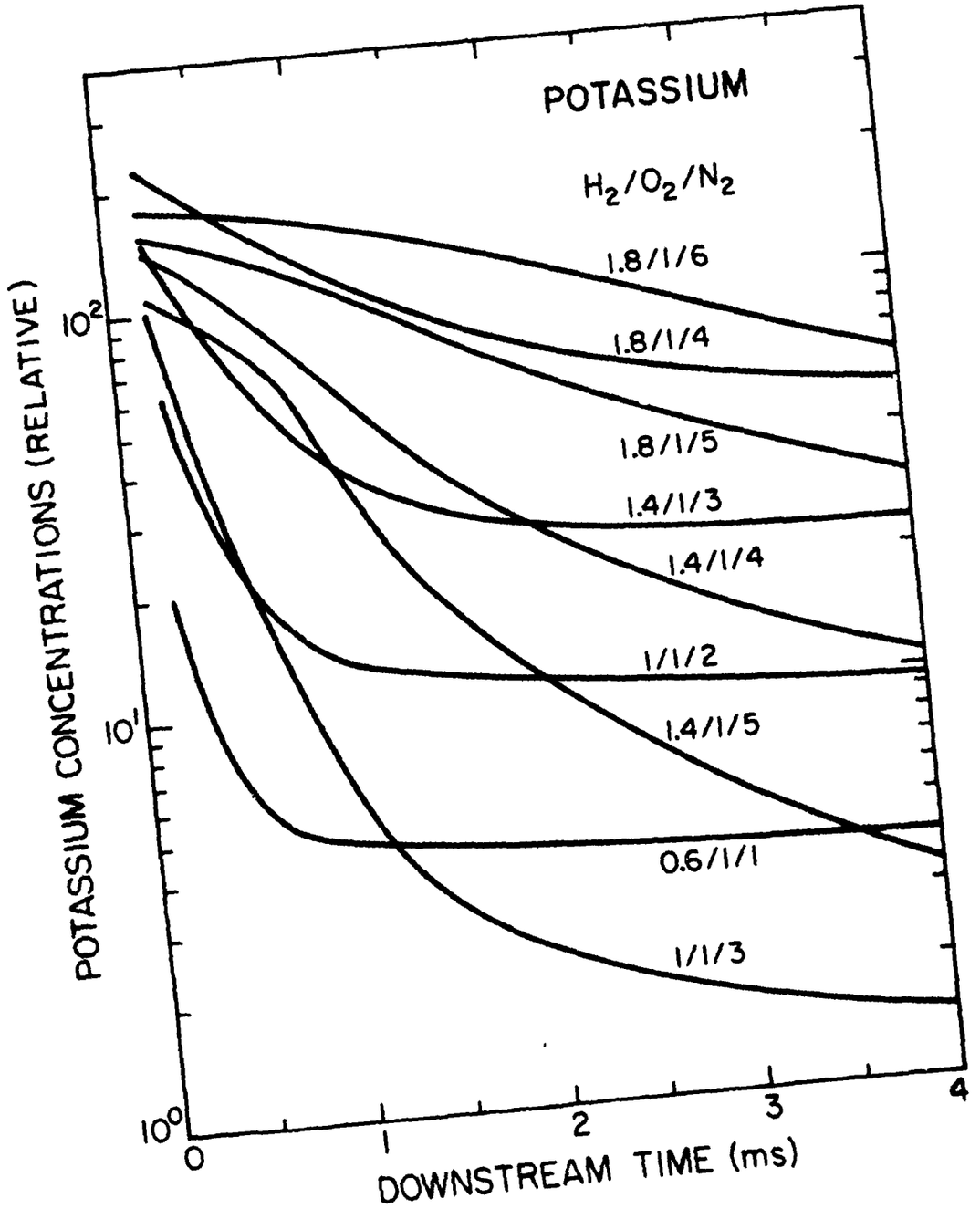


Figure 2. Measured decays of atomic lithium concentration in the burnt gases of a series of oxygen rich flames.

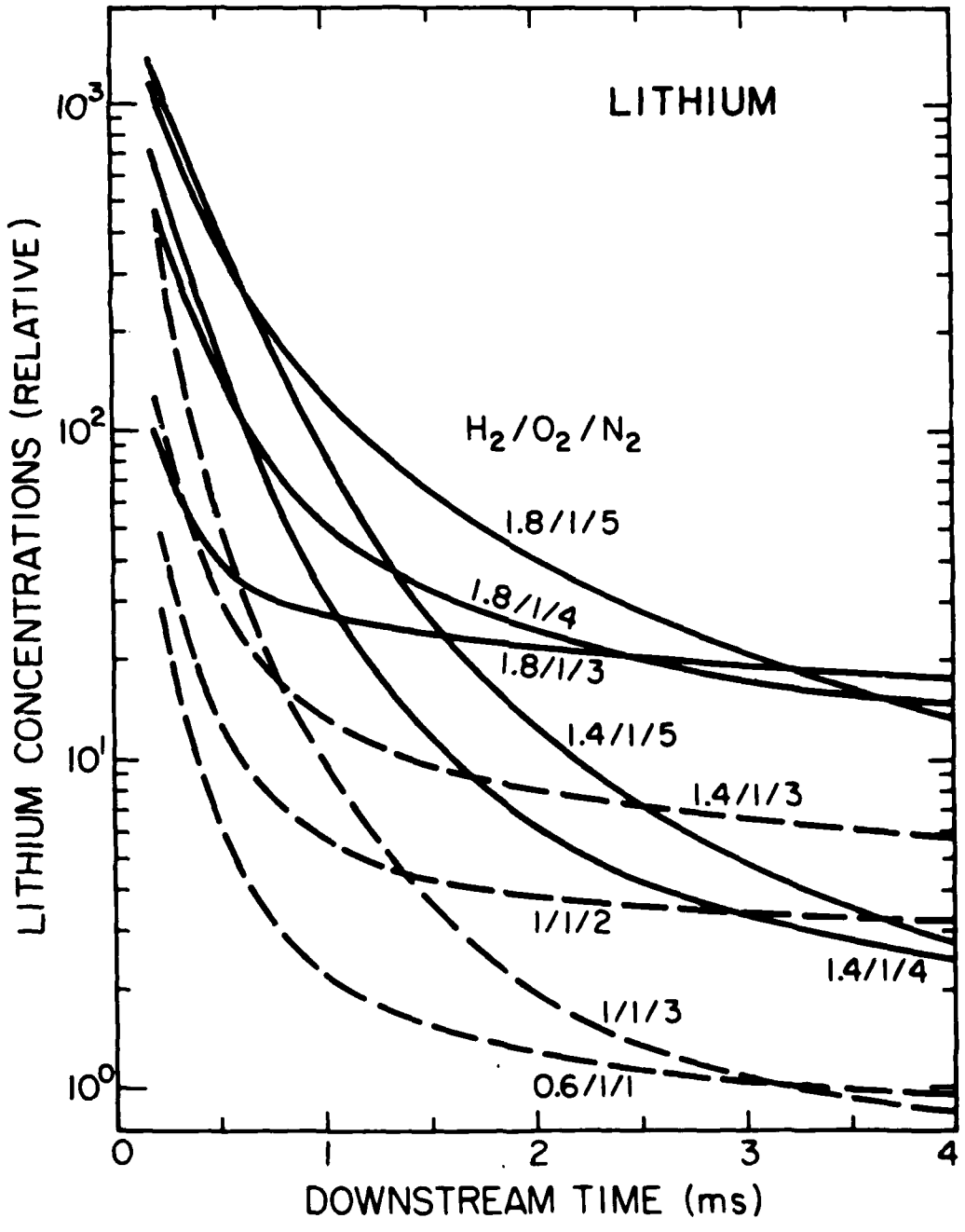


Figure 3. Test for the equilibration of $K+H_2O=KOH+H$ in various fuel lean $H_2/O_2/N_2$ flames. Points refer to times of 0.25 to 4 ms in the burnt gases.

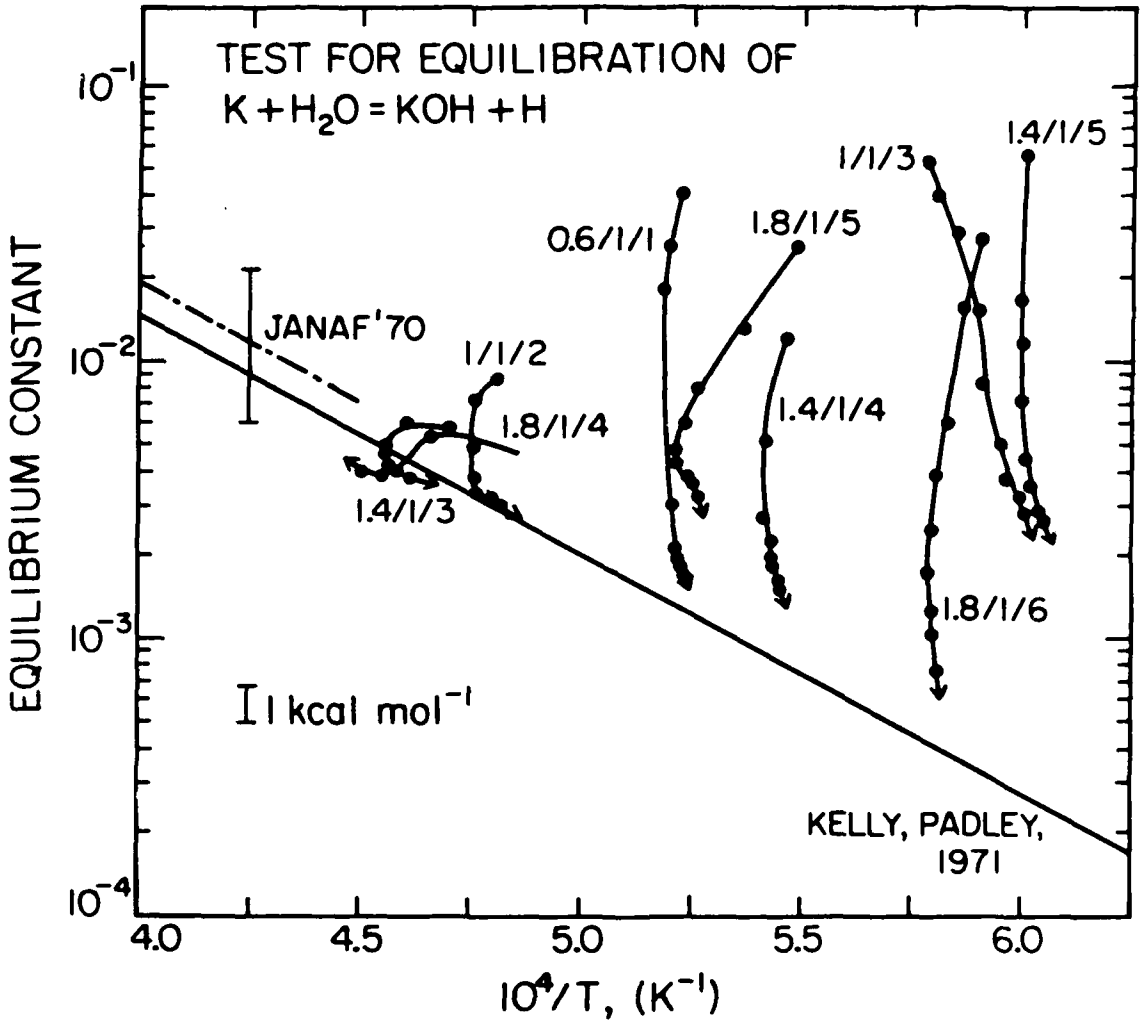
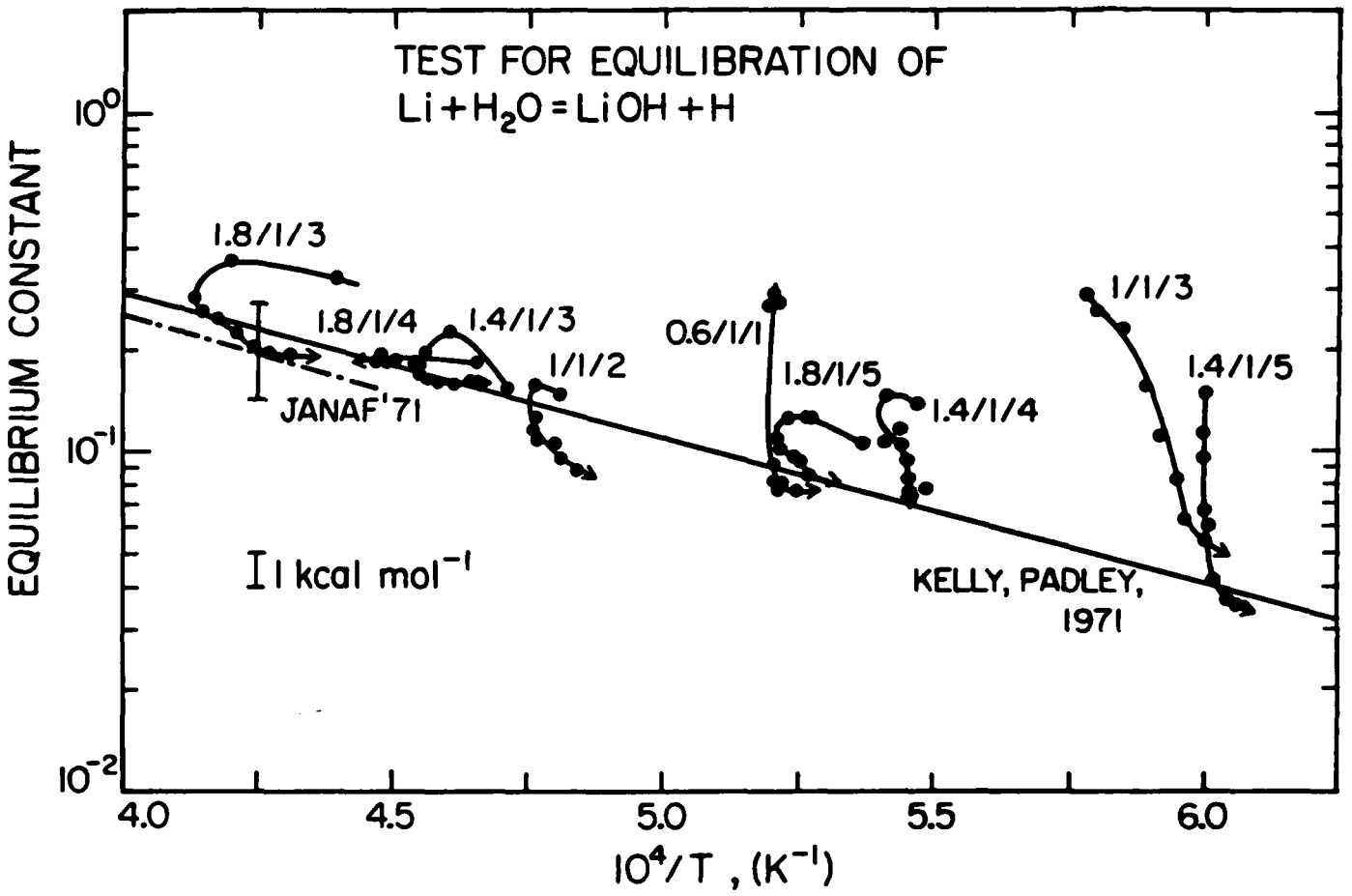


Figure 4. Corresponding plot to the preceeding figure but for $Li+H_2O=LiOH+H$.



a slight adjustment and have been fixed in the present studies to within ±1 kcal mol^{-1}.

The deviations from this balance result from additional kinetic channels which have sufficient kinetic fluxes to perturb the distribution. This role is played by the MO_2 molecule which is formed by a very efficient termolecular reaction,

$$M + O_2 + Z = MO_2 + Z.$$

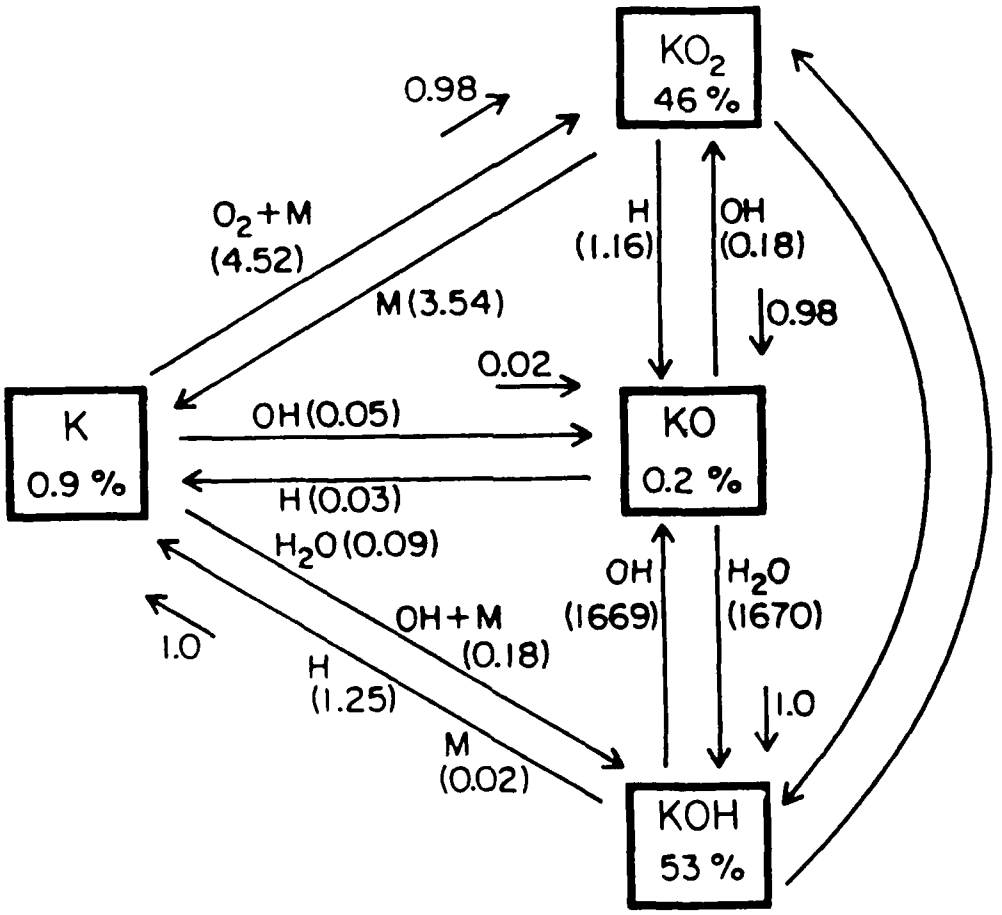
This is unusual in that its fluxes can be comparable to normally encountered bimolecular reactions due to the large rate constant and the concentrations of O_2.

Table 1. Bond dissociation energies of alkali hydroxides and dioxides, D_0 kcal mol^{-1}.

	M-OH			$M-O_2$
	JANAF 1970-1971	Kelley, Padley[4] 1971	Present Date	Present Date
Li	102.8 ± 1.5	103.5 ± 2	103 ± 1	72 ± 5
Na	81.5 ± 3	78.9 ± 2	78.5 ± 1	58 ± 5
K	85.4 ± 3	84.1 ± 2.5	83.5 ± 1	59 ± 5

The kinetic network found to be consistent with the data for all these alkalis is illustrated in Figure 5. Fortunately it is noted that only five or six key reactions play a role from the numerous channels that can be considered. The direct conversion of K to KOH via reaction with H_2O is kinetically constrained due to its endothermicity. An indirect channel via KO_2 is extremely efficient and provides a means of producing KOH. A steady state distribution is rapidly established and is illustrated in Figure 5 for the 2 ms region of one of the flames together with the relative magnitudes of

Figure 5. The relative kinetic fluxes and the overall net flux movements connecting the various potassium species in flame $H_2/O_2/N_2$ (1/1/3) at 2 ms downstream time.



the connecting fluxes for the major reaction channels. The fluxes connecting KO and KOH are extremely large and lock their concentrations in balance and show the small resulting KO levels. In this flame, oxidation is primarily to KO_2 with smaller contributions from the $K+H_2O$ and K+OH+Z reactions. Regeneration of K atoms is either from KOH+H or the thermal dissociation of KO_2. It soon became apparent that the limited capability of H atom to regenerate K atoms places significant importance on the role played by the thermal dissociation of the KO_2 channel and introduces a great sensitivity to the value used for its dissociation energy. The magnitudes of $D_0(M\text{-}O_2)$ now have been reliably fixed and for this reason a rigorous analysis has been continuing to ensure the consistency of our interpretation of the kinetics of these systems in light of the unexpectedly large values that are implied by the data.

In the sodium and potassium cases one complication that arises is due to the role played by the other unusually efficient reaction,

$$Na + OH + Z \rightarrow NaOH + Z.$$

This provides an additional channel to MOH and its importance cannot be independently fixed by the analysis. However, in the case of lithium this channel can play no role due to the already large Li to LiOH fluxes produced by the reaction with H_2O. As a result, this provides more weight for accepting the other analyses which permit the rate constant of the M+OH+Z reaction to vary only within certain bounds that are compatible with its measured lower temperature values quoted in the literature with differing third bodies.

Using rate constants that are compatible with lower temperature independent measures for all the major reactions indicates that it is possible

to reproduce the flame profiles extremely well in all cases and the necessary bond dissociation energies for the MO_2 molecules are listed in Table 1. More stable than previously considered, even though very reactive a significant portion of the alkali can be bound in the MO_2 form.

Most importantly is the insight provided by the fluxes shown in Figure 5. It is noted that oxidation of potassium is mainly by O_2 (and H_2O at higher temperatures) yet regeneration is by thermal dissociation or reaction with H atoms. As noted, the overall flux shows the changes $K \rightarrow KO_2 \rightarrow KO \rightarrow KOH \rightarrow K$ and in so doing destroy H-atoms. In other words catalytic kinetic cycles can be written for which larger concentrations of alkali would significantly modify the flame radical levels.

In summary, as a result of this program, additional data were collected for sodium and new data for the other alkali metals. A rigorous analysis of the kinetics including the need for rate constants to conform with their equilibrium constants has led to a reassessed value for $D_0(Na\text{-}O_2)$ and new values for the other alkalis.

The necessary rate constants required to reproduce the data are consistent with literature values obtained at lower temperatures in N_2 atmospheres. The major species of the present flames are H_2O, N_2 and O_2 and no significantly different efficiencies are apparent for the three body reactions with either N_2, H_2O or O_2 as collision partners.

THE RATE CONSTANT FOR THE REACTION $O + NaO = Na + O_2$

Recently, Plane and Husain[5] have measured the rate constant for this reaction. NaO was produced by titrating Na with N_2O and the reaction with O-atom was followed by monitoring the chemiluminescent emission from that part branching to the excited $Na(^2P)$ product. At first sight their rate constant value of 3.7×10^{-10} cm^3 $molecule^{-1}s^{-1}$ at 573 K appears a normal magnitude. However, by

utilizing the well established equilibrium constant, the implied rate constant for the reverse $Na+O_2$ reaction,

$$k=2.4x10^{-8}exp(-59310/RT)$$

is seen to have a preexponential factor that is about 54-fold greater than expected for normal gas kinetic collisions and an energy barrier equal to the reaction enthalpy. Analyses are endeavoring to establish the reliability of this measure. Although it is know that certain alkali atom/halogen reactons, while presumably are also highly ionic in nature, can also exhibit larger than expected cross sections, this is usually by only a factor of several-fold. Moreover, corresponding reactions such as $Na+O_3$ [6], $Na+N_2O$ [6], $Na+H_2O$ [7] and $Li+H_2O$ [7,8] show normal gas kinetic type cross sections.

It is interesting to note that if this reaction is entered into our model with such a large cross section the kinetic fluxes connecting Na and NaO still are not sufficient to perturb the distribution controlled by the other major reactions.

THE SODIUM/LITHIUM METHOD FOR ABSOLUTE H-ATOM MEASUREMENTS

An effective method for independently measuring H-atom concentrations in flames is the so called Na/Li method.[9] This has been used extensively in fuel-rich flames and is based on comparing the relative emission intensities from know additions of sodium and lithium. Its premise is that sodium is essentially inert in such an environment and lithium is distributed only between Li and LiOH. Numerous studies skirted with the concept of extending its use also to fuel-lean flames[10,11] but it was realized that this was fraught with uncertainties due to the then unknown behavior in such environments. We are now in a position to quantitatively predict the errors of such an application. In fact the conclusions illustrate the sound judgment not to extend its operational regime because although varied, sometimes too

small, sometimes too large, errors would be as large as 30-fold in the flames studied in the present program.

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PRESENTATIONS

1. "Detailed High Temperature Oxidation Chemistry of the Alkali Metals in Flames", Presented at the "Workshop on the Chemical Suppression of Rocket Afterburning and of Gun Muzzle Flash", Ballistic Research Laboratory, Aberdeen Proving Ground, MD, June 11-12, 1986.

2. "The High Temperature Chemistry and Thermodynamics of Alkali Metals (Lithium, Sodium and Potassium) in Oxygen-Rich Flames", M. Steinberg and K. Schofield, Presented at the Fall Joint Technical Meeting of the Western States and Japanese Sections of the Combustion Institute, Honolulu, HI, November 22-25, 1987.

PUBLICATIONS

1. "The Chemical Kinetics and Thermodynamics of Lithium Species on Oxygen-Rich Hydrogen Flames", M. Steinberg and K. Schofield (to be submitted to the Journal of Chemical Physics).

2. "A Reassessment of the Bond Strength of NaO_2 and its Chemical Kinetics in Oxygen-Rich Hydrogen Flames", M. Steinberg and K. Schofield (to be submitted to the Journal of Chemical Physics).

3. "The High Temperature Chemistry and Thermodynamics of Alkali Metals (Lithium, Sodium and Potassium) in Oxygen-Rich Flames", M. Steinberg and K. Schofield, Paper WSS/CI 3A-042, Extended Abstract, Fall Joint Technical Meeting of the Western States and Japanese Sections of the Combustion Institute, Honolulu, HI, November 22-25, 1987.

4. "A Reexamination of the Na/Li Method for Measuring H-Atom Concentrations in Flames: Applicable Regimes and Error Estimates", M. Steinberg and K. Schofield (to be submitted to Combustion and Flame).

5. "The Chemical Kinetics and Thermodynamics of Potassium Species in Oxygen-Rich Hydrogen Flames", M. Steinberg and K. Schofield (to be submitted to the Journal of Chemical Physics).

6. "Implications of the Rate Constant Measurement for the $O+NaO=Na+O_2$ Reaction", M. Steinberg and K. Schofield (to be submitted to the Int. Journal of Chemical Kinetics).

7. "The Chemical Kinetics and Thermodynamics of Rubidium Species in Oxygen-Rich Hydrogen Flames", M. Steinberg and K. Schofield (to be submitted to the Journal of Chemical Physics).

8. "The Chemical Kinetics and Thermodynamics of Cesium Species in Oxygen-Rich Hydrogen Flames", M. Steinberg and K. Schofield (to be submitted to the Journal of Chemical Physics).