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LASER FLUORESCENCE STUDIES OF THE CHEMICAL INTERACTIONS OF SODIUM SPECIES WITH SULFUR BEARING FUELS

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ABSTRACT

By using a large matrix of fuel rich and fuel lean $\text{H}_2/\text{O}_2/\text{N}_2$ and fuel rich $\text{C}_2\text{H}_2/\text{O}_2/\text{N}_2$ flames, the behavior of sodium and its interactions with sulfur at high temperatures have been extensively characterized. OH concentrations have been measured for each flame using the previously validated laser induced fluorescence technique. Sodium atomic concentrations were obtained by the saturated laser fluorescence method. Measurements were made in the absence and presence of up to 2% sulfur. Part of the data now have been fully analyzed, however the sulfur systems still await a complete analysis. At present, the following conclusions are apparent.

In oxygen rich systems sodium is depleted by $\text{NaO}_2$ and $\text{NaOH}$ formation. The relative amounts of each are controlled by the degree of non-equilibration of the flame radicals and by the temperature. The bond strength of $\text{NaO}_2$ has been established. A preliminary paper was presented recently, a copy of which is appended. A more detailed paper is to be submitted to the J. Chem. Physics.

For the first time, a complete understanding of the complex behavior of sodium in fuel-lean $\text{H}_2/\text{O}_2$ flames has emerged and computer modeling has permitted various rate constants of Na, $\text{NaO}_2$ and $\text{NaOH}$ reactions to be approximately fixed. $\text{NaO}$ is shown to play only a very minor role and $\text{NaH}$ is entirely negligible. Previous investigations and interpretations of these systems have been shown to be largely in error.

The magnitudes of the additional depletion of sodium and the reduced concentrations of OH in the presence of various levels of sulfur have been recorded. In fuel-rich flames, sodium exists predominantly as free Na with small amounts of $\text{NaOH}$. In oxygen-rich conditions Na and $\text{NaOH}$ can occur in significantly varying distributions. The steady-state concentration levels of $\text{NaO}_2$ and $\text{NaO}$ generally are much smaller. Consequently, at first sight it might be expected that the sulfur species that have been suggested as forming under these conditions, namely either $\text{NaS}$, $\text{NaSH}$, $\text{NaSO}_2$ or $\text{NaSO}_3$ most probably originate from Na or $\text{NaOH}$. 
In all cases, adding sulfur to the flames catalyzes the rate of recombination of the excess flame radicals.

The relative magnitudes of the sulfur addition effects on Na and OH concentration levels are most interesting. Enhanced sodium depletions are quite significant for both fuel-rich and lean hydrogen flames but show little if any change for the fuel-rich acetylene flame series. However, enhanced radical rates of decay of OH are very pronounced in both these acetylene flames and the fuel rich hydrogen flames yet are much reduced in the lean hydrogen flames. Flame modeling of both the Na/S interactions and the catalytic kinetic schemes explaining the radical decays will be put to a severe test in describing this large set of flame data.
INTRODUCTION

The aim of this program has been to identify and characterize the basic flame chemistry which is the precursor to the formation of \( \text{Na}_2\text{SO}_4 \) in sodium and sulfur bearing flames. The study is to complement the previous NASA Lewis program \(^1\text{–}^3\) which has identified \( \text{NaSO}_2 \), \( \text{NaSO}_3 \) and \( \text{Na}_2\text{SO}_4 \) by mass spectroscopic analyses of the burnt gases of methane/oxygen flames at longer times. This has been successfully achieved using a large number of fuel rich and lean \( \text{H}_2/\text{O}_2/\text{N}_2 \) and fuel rich \( \text{C}_2\text{H}_2/\text{O}_2/\text{N}_2 \) flames which span a significant temperature regime and have widely differing compositions. The flames have been characterized using laser fluorescence techniques. The data, not yet completely analyzed, provide important contributions in the following three main areas:

- Resolve the chemical nature of sodium in oxygen rich flames and establish the bond strength of \( \text{NaO}_2 \).
- Identify the chemistry of the sodium/sulfur interactions for both fuel-rich and fuel-lean conditions and derive thermo-chemical data for the dominant species.
- Characterize the chemical kinetics of the catalytic chains, which enhance the \( \text{OH} \) radical decays in the presence of sulfur, for both fuel-rich and fuel-lean conditions.
FLAME MATRIX

Experimental conditions are outlined in the attached paper. In addition to the ten oxygen-rich flames, ten fuel-rich $\text{H}_2/\text{O}_2/\text{N}_2$ and seven fuel-rich $\text{C}_2\text{H}_2/\text{O}_2/\text{N}_2$ also were studied. Their temperatures similarly spanned the 1700 to 2400 K temperature range. Compositions were chosen such as to give significant variations in the $\text{H}_2$, $\text{CO}$, $\text{CO}_2$ and $\text{H}_2\text{O}$ major species concentrations as well as a pronounced variation among the $\text{OH}$, $\text{H}$, $\text{O}$ and $\text{O}_2$ minor species. It is these variations in the large number of flames which help to unravel the nature of the chemistry involved.

Each flame contained traces of sodium at initial input levels corresponding to about $10^{10}$ cm$^{-3}$. 0%, or approximately 1% or 2% of sulfur was added to the flames as $\text{H}_2\text{S}$ or $\text{SO}_2$. $\text{H}_2\text{S}$ is added to rich flames and $\text{SO}_2$ is added to lean flames to avoid any significant thermal effects which would result if the ordering of the $\text{H}_2\text{S}$ and $\text{SO}_2$ additions were reversed. A data base for the sulfur chemistry was already available for the 3/1/4, 5, 6 and 4/1/4, 5, 6 flames with 0.25, 0.5, and 1.0% $\text{H}_2\text{S}$ additions. Measurements of each flame property were made at several heights above the burner to cover flow times of about 4 ms. The $\text{H}_2/\text{O}_2/\text{N}_2$ (4/1/2) flame containing 1% $\text{H}_2\text{S}$ is included in the flame matrix to calibrate the OH fluorescence measurements. This high temperature flame reaches its equilibrium plateau very rapidly, within 2 to 3 cm of the burner. The presence of the sulfur increases the rate of attainment of equilibrium by catalyzing the $\text{H}$ and $\text{OH}$ recombination. From measurements of temperature in the plateau region the number densities of all species can be calculated using the NASA equilibrium program along with updated thermodynamic properties for participating species. In this way the OH relative concentrations were scaled absolutely.
MEASUREMENTS

The temperatures of all these flames have been measured with and without sulfur, as a function of distance downstream in the burnt gases using the sodium D-line reversal method. An extensive effort was made to ensure that these were as exact as possible. The final values are considered to be precise to \( \pm 25^\circ \).

Burning velocities are such that flame lengths equivalent to times of up to 4–5 ms provide reliable data that is not affected by entrained air effects.

Quantitative atomic fluorescence measurements at low laser powers are not possible unless a constant quenching environment exists. Consequently, because we were examining flames with a wide variety of composition, it was necessary to obtain sodium fluorescence data that could be quantitatively related to concentrations by operating in a saturated mode. By using the short laser pulse length of a high power Nd. Yag Quanta Ray laser we have validated that the fluorescence intensities do reflect the sodium concentration and that potential problems such as laser induced chemistry and ionization are negligible.

Previously, we have validated a quantitative laser fluorescence technique for monitoring OH concentrations in flames and applied this to unravelling the chemistry of sulfur in H\(_2\)-rich flames. Using this method, OH fluorescence intensities have been measured throughout each of the twenty seven H\(_2\)/O\(_2\)/N\(_2\) and C\(_2\)H\(_2\)/O\(_2\)/N\(_2\) flames used in this study. At present, this is the only reliable method available for measuring OH in a sulfur flame environment. Previous studies on the Na/S interactions have not measured the radical concentrations.

A kinetic analysis indicates that the detailed balances between the hydrogen/oxygen flame radicals, which are well established for fuel-rich flames, similarly are likely to exist for fuel-lean flames on the millisecond time scales examined here. Consequently, in all cases, it is possible to use the measured OH concentrations along with the major stable species
which are known from equilibrium code calculations, to derive the concentrations of the other trace species. For fuel rich conditions, the radicals are related via the following proportionalities:

\[ [\text{OH}] \propto [\text{H}] \propto [\text{O}]^{1/2} \propto [\text{O}_2]^{1/2}. \]

In fuel-lean conditions, these become modified to

\[ [\text{OH}] \propto [\text{H}]^{1/3} \propto [\text{O}]^{1/2} \propto [\text{H}_2]^{1/2}. \]

Consequently, flame profiles for all the basic species in the H\(_2\)/O\(_2\) systems are established and are the invaluable aid that is required to unravel more complicated flame chemistries.
Sodium Chemistry in Sulfur-Free Flames

Under fuel-rich conditions, and for temperatures less than about 2400 K, sodium is unreactive. It ionizes to a very small extent on the millisecond time scale and forms only slight amounts of NaOH. NaH, NaO, and NaO₂ are entirely negligible under these conditions. Consequently, the sodium remains in its free atomic state, its concentration decaying slightly with time due to diffusional losses. It has been examined many times before and is regarded as being reasonably well understood for fuel-rich conditions. However, the case for oxygen-rich flames was in a very different situation at the start of this program. The nature of the sodium depletion in such cases had only been examined in several preliminary studies and was in a very unsatisfactory state as to the nature of the sodium species formed and their specific roles.

It became apparent, that before any analysis of Na/Sulfur interactions could be considered, it was first necessary to better characterize this behavior of sodium in sulfur-free oxygen-rich flames. Fortunately, this has been possible and a preliminary paper outlining the importance of NaOH, NaO₂ and NaO is appended. This has clearly defined the importance of NaOH as the major species, established the thermochemistry of NaO₂, and illustrates the important role played by this somewhat unstable species. A more complete paper presently is being written. The chemical reactions of sodium that were considered are represented in Figure 1 and the specific enthalpies and final set of rate constants are listed in Table I. For convenience, notes on the specific values are attached to Table II. The fluxes connecting Na to NaO are so small and those connecting NaO to NaOH so large that we are insensitive to these reaction rate constants and can only specify upper limits.
Table I. Potential Reactions of Na, NaO, NaO₂ and NaOH in H₂/O₂ Flames

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH° 2000K kcal mol⁻¹</th>
<th>Forward Reaction</th>
<th>Reverse Reaction</th>
</tr>
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<tbody>
<tr>
<td>1, -1 Na+O₂+M=NaO₂+M</td>
<td>-(0.69±D°₀)</td>
<td>1.8×10⁻²⁸T⁻¹</td>
<td>2.2×10⁻¹¹T⁻¹/²exp[(-(685+D°₀)/RT)]</td>
</tr>
<tr>
<td>2, -2 NaO₂+H=Na+HO₂</td>
<td>-(54.04+D°₀)</td>
<td>1.7×10⁻¹²T¹/²</td>
<td>1.2×10⁻¹²T¹/²exp[(-(46,450-D°₀)/RT)]</td>
</tr>
<tr>
<td>3, -3 NaO₂+H=NaO+OH</td>
<td>-(46.45-D°₀)</td>
<td>7.4×10⁻¹²T¹/²</td>
<td>1.6×10⁻¹³T¹/²exp[(-(62,010-D°₀)/RT)]</td>
</tr>
<tr>
<td>4, -4 NaO₂+O=NaO+O₂</td>
<td>-(62.01-D°₀)</td>
<td>8.2×10⁻¹⁴T¹/²</td>
<td>-</td>
</tr>
<tr>
<td>5, -5 NaO₂+OH=NaOH+HO₂</td>
<td>+(D°₀-10.25)</td>
<td>1.5×10⁻¹³T¹/²exp[(-(D°₀-10,250)/RT)]</td>
<td>-</td>
</tr>
<tr>
<td>6, -6 NaO₂+H=NaOH+O</td>
<td>-(62.47-D°₀)</td>
<td>1.4×10⁻¹³T¹/²</td>
<td>8.4×10⁻¹⁴T¹/²exp[(-(62,470-D°₀)/RT)]</td>
</tr>
<tr>
<td>7, -7 NaO₂+OH=NaO₂+O₂</td>
<td>-(78.03-D°₀)</td>
<td>2.8×10⁻¹⁴T¹/²</td>
<td>2.0×10⁻¹³T¹/²exp[(-(78,030-D°₀)/RT)]</td>
</tr>
<tr>
<td>8, -8 NaOH+OH=NaO+H₂O</td>
<td>-0.62</td>
<td>≤1.0×10⁻¹¹T¹/²</td>
<td>≤2.6×10⁻¹¹T¹/²exp(-624/RT)</td>
</tr>
<tr>
<td>9, -9 NaOH+H=NaO+H₂</td>
<td>+14.04</td>
<td>≤7.4×10⁻¹¹T¹/²exp(-14,040/RT)</td>
<td>≤4.6×10⁻¹¹T¹/²</td>
</tr>
<tr>
<td>10, -10 NaOH+O=NaO+OH</td>
<td>+16.02</td>
<td>≤2.1×10⁻¹¹T¹/²exp(-16,020/RT)</td>
<td>≤5.7×10⁻¹²T¹/²</td>
</tr>
<tr>
<td>11, -11 NaOH+O₂=NaO+HO₂</td>
<td>+67.78</td>
<td>≤2.0×10⁻¹¹T¹/²exp(-67,775/RT)</td>
<td>-</td>
</tr>
<tr>
<td>12, -12 Na+H₂O=NaOH+H</td>
<td>+44.41</td>
<td>2.8×10⁻¹¹T¹/²exp(-44,410/RT)</td>
<td>1.1×10⁻¹²T¹/²</td>
</tr>
<tr>
<td>13, -13 Na+OH+M=NaOH+M</td>
<td>-78.71</td>
<td>≤7.0×10⁻²⁹T⁻¹</td>
<td>2.4×10⁻¹¹T¹/²exp(-78,710/RT)</td>
</tr>
<tr>
<td>14, -14 Na+HO₂=NaOH+O</td>
<td>-8.43</td>
<td>-</td>
<td>4×10⁻¹⁵T¹/²exp(-8,430/RT)</td>
</tr>
<tr>
<td>15, -15 Na+OH=NaO+H</td>
<td>+43.78</td>
<td>≤1.8×10⁻¹¹T¹/²[(-43,780/RT)]</td>
<td>≤1.8×10⁻¹²T¹/²</td>
</tr>
<tr>
<td>16, -16 Na+HO₂=NaO+OH</td>
<td>+7.59</td>
<td>-</td>
<td>≤2.7×10⁻¹³T¹/²</td>
</tr>
<tr>
<td>17, -17 Na+O₂=NaO+O</td>
<td>+59.34</td>
<td>≤1.7×10⁻¹¹T¹/²exp(-59,340/RT)</td>
<td>≤1.5×10⁻¹³T¹/²</td>
</tr>
</tbody>
</table>

Reaction number: +forward reaction, - reverse reaction.

D°₀ represents D°₀(Na-O₂): Optimum Fit for 35.0 kcal mol⁻¹.
ΔHf(NaO)⁽¹⁸⁾, ΔHf(NaOH)⁽¹²⁾, R = 1.9872 cal deg⁻¹.
Table II. Notes on the Preexponential Terms of the Rate Constants Listed in Table I.

1. Husain and Plane's value at 800K was given a $T^{-1}$ dependence and optimized by computer fit, i.e., $k_1 = 8 \times 10^{-28} \ T^{-1} \ \alpha$, which gave $\alpha = 0.23$.

-1. Hard sphere gas kinetic value $\times \beta$. Computer fit gave $\beta = 1$.

2. Gas kinetic (G.K.) value, modified by the equilibrium constant (i.e. the reverse reaction is gas kinetic). This limits its maximum value to $2.3 \times 10^{-2} \ G.K.$ which appears acceptable.

3. Gas kinetic value $\times \delta$. Computer fit gives $\delta = 0.1$.

-3. Gas kinetic value, modified by the equilibrium constant $\times \delta$. $k_{-3} = 0.7 \times G.K. \times \delta$, $\delta = 0.1$.

4. Gas kinetic value, modified by the equilibrium constant $\times \eta$. Computer fit gives $\eta = 0.01$. $k_4 = 0.4 \times G.K. \times \eta$.

-4. Gas kinetic value $\times \eta$. $\eta = 0.01$.

5. Gas kinetic value, modified by the equilibrium constant $\times \phi$. Computer fit gives $\phi = 0.01$. $k_5 = 0.7 \times G.K. \times \phi$.

6. Gas kinetic value modified by the equilibrium constant and by a factor of $4 \times 10^{-3}$ (from the branching ratios of analogous H+HO$_2$ reactions). It seems an unlikely channel. $k_6 = 0.5 \times G.K. \times 4 \times 10^{-3}$.

-6. Gas kinetic value $\times 4 \times 10^{-3}$.

7. Gas kinetic value, modified by the equilibrium constant $\times \psi$. Computer fit gives $\psi = 0.01$. $k_7 = 0.13 \times G.K. \times \psi$.

-7. Gas kinetic value $\times \psi$.

8. Gas kinetic value, modified by the equilibrium constant. $k_8 = 0.45 \times G.K.$ Our model is insensitive to its true value.

-8. Gas kinetic value. Our model is insensitive to its true value

9. Gas kinetic value. Our model is insensitive to its true value.

-9. Gas kinetic value, modified by the equilibrium constant. $k_{-9} = 0.8 \times G.K.$ Our model is insensitive to its true value.
10. Gas kinetic value. Our model is insensitive to its true value.

11. Gas kinetic value. Our model is insensitive to its true value.

12. Gas kinetic value.

13. Jensen and Jones' value \( k_{13} = 5 \times 10^{-27} T^{-1} \). Computer fits indicate that this cannot be permitted to make any significant contribution. \( \gamma = 0.014 \). Appears to be analogous to H+OH+M.

14. Gas kinetic value, modified by the equilibrium constant and by a factor of \( 4 \times 10^{-3} \) (from the branching ratios of analogous H+H,O reactions). It appears to be a negligible channel. \( k_{14} = 5 \times 10^{-2} \times G.K. \times 4 \times 10^{-3} \).

15. Gas kinetic value. Our model is insensitive to its true value due to the small fluxes.

16. Gas kinetic value, modified by the equilibrium constant. \( k_{16} = 1.6 \times 10^{-2} \times G.K. \).

17. Gas kinetic value. Our model is insensitive to its value due to the small fluxes.

Reactions -2, -5, -11, 14 and 16 were not included in the model due to their low fluxes and insignificance. These all involved reactions with H,O.2.
Computer fits to the two highest temperature flames, in which NaOH is predicted to be dominant, indicate a pronounced preference for the lower $D_0^0$ (Na-OH) value of Kelley and Padley\textsuperscript{12} over that of the JANAF Tables.

Under oxygen-rich conditions the predominant species produced is NaOH. However, depending on the flame this is either directly from Na or via NaO\textsubscript{2} or NaO. In lower temperature flames the steady-state concentration of NaO\textsubscript{2} can become significant.

Our understanding of this system now is on a firm base and should permit a meaningful interpretation of the additional depletion processes on the addition of sulfur.

**Sodium Chemistry in Sulfur-Bearing Flames**

Two previous studies have examined these systems but came to conflicting conclusions. Fenimore\textsuperscript{8} observed a decrease in Na with increased addition of SO\textsubscript{2} to rich and lean H\textsubscript{2}-Air flames which he found consistent with the rapid equilibrium of

$$\text{NaOH} + \text{SO}_2 = \text{NaSO}_2 + \text{OH}.$$  

In C\textsubscript{3}H\textsubscript{8}/O\textsubscript{2}/N\textsubscript{2} flames Durie et al.\textsuperscript{9} reported different reaction paths in the rich and lean systems. NaS and NaSO\textsubscript{3} were identified as the primary Na-S products in rich and lean flames respectively,

$$\text{NaOH} + \text{S} = \text{NaS} + \text{OH}$$
$$\text{NaOH} + \text{SO}_3 = \text{NaSO}_3 + \text{OH}.$$  

Clearly, the situation is in a similar unsatisfactory state as was the sodium/oxygen lean flame chemistry. All possible chemical interactions must be considered for both fuel-rich and lean cases in order to establish whether NaSO\textsubscript{2}, NaSO\textsubscript{3}, NaS or NaSH is of importance. None of these have thermochemical values that have been characterized.
The data reduction will be undertaken when time permits. Such efforts are being completed on a voluntary basis due to the absence of continued financial support.

a) Fuel Rich H$_2$/O$_2$/N$_2$ Flame Data

In the presence of up to 2% H$_2$S each of the sodium concentration flame profiles is decreased. At 3 ms the extent of the depletion ranges from about 7.5 up to 46% in the various flames. The corresponding profiles of OH concentrations show more pronounced decreases ranging from 1.5 up to 7 fold. No direct correlation is apparent but the three series of constant H$_2$/O$_2$ ratios with differing flame N$_2$ content each reflect larger decreases of Na and OH as temperatures decrease. Figures 2 and 3 indicate the changes observed in several representative flames.

b) Fuel Rich C$_2$H$_2$/O$_2$/N$_2$ Flame Data

Rather curiously, addition of up to 2% H$_2$S has little if any effect on the sodium profiles of fuel-rich acetylene flames. Although their flame temperatures do not span as large a range as the hydrogen flames, ranging from 1900 to 2500 K, there is a sufficient temperature overlap to indicate that this is not due solely to temperature. The sulfur drastically modifies the radical concentrations, as indicated in Figure 3, and it is difficult to predict the source of this changed behavior between the acetylene and hydrogen fueled series of flames. Nevertheless, this apparent absence of any pronounced depletion of the sodium will have to be consistent with the hydrogen fuel-rich model.

c) Fuel Lean H$_2$/O$_2$/N$_2$ Flame Data

Metal-Oxygen bonds tend to be consistently stronger than those of metal-sulfur. Consequently, the additional depletion of sodium that is observed when sulfur is added to oxygen rich hydrogen flames is somewhat unexpected. At 3 ms it ranges from a very small effect in the 1/1/2 flame up to about a 70% decrease in the amount of free sodium, over that when sulfur is not present, in such flames as the 1.4/1/5 and 1.8/1/6. Moreover, as indicated in Figure 3, the catalytic decrease in the radical concentrations is much less pronounced in the oxygen-rich media and corresponding OH concentrations decrease at the very most by only 50%.
Figure 2. Atomic Sodium Concentrations Derived from Saturated Laser Fluorescence in Various Lean and Rich Hydrogen Flames With and Without Sulfur.
Figure 4. OH Fluorescence Intensities in Three Flames of Similar Temperature (2150K) With and Without 1% Sulfur Addition.
Obviously, comparisons of these large data blocks in the three differing flame media should be of considerable help in resolving the nature of the interactions that are occurring.

The Catalytic Effect of Sulfur on Flame Radical Recombination

As mentioned briefly above, and indicated in Figure 3, the rate of decay of OH throughout the burnt gases is enhanced by the presence of sulfur in all three fuel/oxidant series of flames. Additional catalytic mechanisms became available to recombine the excess radical concentrations and shorten the time for their decays toward the equilibrium values. This effect has been studied by several groups for fuel-rich conditions and the following mechanisms suggested,

\[ H + SO_2 + M \rightarrow HSO_2 + M \]

or

\[ OH + SO_2 + M \rightarrow HSO_3 + M \]

followed by

\[ H + HSO_2 \rightarrow H_2 + SO_2 \]

or

\[ OH + HSO_2 \rightarrow H_2O + SO_2 \]

or

\[ H + HSO_3 \rightarrow H_2O + SO_2 \]

which alternatives are difficult to distinguish in hydrogen rich flames. In fuel-lean flames, only Fenimore and Jones have discussed its effect and suggested

\[ O + SO_2 + M \rightarrow SO_3 + M \]

\[ O + SO_3 \rightarrow O_2 + SO_2 \]

or

\[ H + SO_3 \rightarrow OH + SO_2 \]

As to whether we can clarify or confirm the fuel-rich mechanism is to be seen. However, there is no doubt we can examine the mechanism under lean conditions in more detail than previously. Due to the importance of OH in oxygen-rich flames it seems unlikely that such a mechanism based on O-atom catalysis will be dominant.
REFERENCES


"The Detailed Chemistry and Thermodynamics of Sodium in Oxygen-Rich Flames," A.J. Hynes, M. Steinberg and K. Schofield, Presented at the Fall Meeting of the Western States Section of the Combustion Institute, Sandia National Laboratories, Livermore CA, October 11-12, 1982.

PUBLICATIONS – IN PREPARATION
A. J. Hynes, M. Steinberg and K. Schofield


APPENDIX

Paper Presented at the Fall Meeting of the Western States Section of the Combustion Institute Held at Sandia National Laboratories, Livermore, October 11 - 12, 1982.