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Chemical Kinetic Studies of Reactions Relevant
to Muzzle Flash and Afterburning Suppression
by Potassium and Sodium Compounds

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FINAL REPORT

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Prepared By:

Mark S. Zahniser, Joel A. Silver, Alan C. Stanton
and Charles E. Kolb

October, 1985

U.S. Army Research Office

Contract No. DAAG 29-81-C-0024

Aerodyne Research, Inc.
45 Manning Road
Billerica, MA. 01821

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Rate constants have been determined for gas phase reactions of alkali species which are relevant to flame suppression chemistry by sodium and potassium compounds. Sources and detection methods for gas phase molecular alkali species KO, KO_2, Na, NaO_2 and NaOH have been developed and applied to kinetic studies of these species using a high temperature fast flow reactor.

Rate constants for the recombination reactions of alkali atoms with molecular oxygen, $K + O_2 + M \rightarrow KO_2 + M$ and $Na + O_2 + M \rightarrow NaO_2 + M$, have been

measured as a function of temperature from 300 to 700 K. Laser induced fluorescence is used to monitor the disappearance of Na or K as a function of O_2 and M. The reactions are studied in their low pressure third order limit from 1 to 8 torr total pressure with N_2, He, and Ar as third bodies.

The reactions of NaOH, NaO_2 and NaO with HCl at 300 K are found to procede at their gas kinetic limits to form NaCl. Other reactions studied include: NaOH + H → Na + H_2O, NaCl + H → Na + HCl and both Na and K with H_2O_2. Product analysis for the latter two shows that for Na 0.6 of the reactions form NaOH + OH with the remainder forming NaO + H_2O while for K the main products are KO + H_2O with less than 2×10^{-3} going to KOH + OH. An upper limit of 3×10^{-15} $cm^3 s^{-1}$ is established for the reaction K + H_2O → KOH + H at 1273 K.

KOH has been detected in the gas phase by infrared absorption at 424 cm^{-1} using a tunable diode laser. This method has wide applicability for direct detection of a number of molecular alkali species for laboratory kinetic studies and for in situ combustion flame diagnostics. Theoretical sensitivity estimates are calculated for KOH, KO_2, KO, NaOH, NaO_2, NaO and NaCl for both high temperature, atmospheric pressure and low pressure flow tube conditions.

TABLE OF CONTENTS

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ABSTRACT

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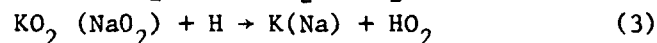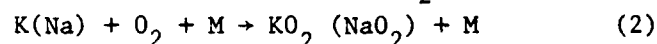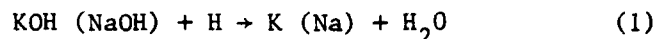
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KOH has been detected in the gas phase by infrared absorption at $424/cm$ using a tunable diode laser. This method has wide applicability for direct detection of a number of molecular alkali species for laboratory kinetic studies and for in situ combustion flame diagnostics. Theoretical sensitivity estimates are calculated for KOH, KO_2, KO, $NaOH$, NaO_2, NaO and $NaCl$ for both high temperature, atmospheric pressure and low pressure flow tube conditions.

1. Statement of Problem Studied

The secondary combustion of CO and H_2 rich propellant exhaust gases from large caliber guns (muzzle flash) and tactical rockets (afterburning) is a basic combustion phenomenon with seriously detrimental characteristics. Propellant formulators have long known that these secondary combustion processes can be suppressed by the addition of sodium and/or potassium salts to the propellant mix.

Modeling of secondary combustion in both rocket and muzzle exhaust flows strongly indicates that this suppression takes place via the scavenging of combustion radical chain carriers (H, OH, HO_2, O) through interactions with gas phase alkali species.[1-5] Key reactions in this scavenging process include:

$$KOH \ (NaOH) + H \rightarrow K \ (Na) + H_2O \qquad (1)$$

$$K(Na) + O_2 + M \rightarrow KO_2 \ (NaO_2) + M \qquad (2)$$

$$KO_2 \ (NaO_2) + H \rightarrow K(Na) + HO_2 \qquad (3)$$

Model calculations indicate that reaction (1) is the major chain radical scavenging reaction operating under rocket exhaust plume or muzzle flow field conditions.[1-5] Model kinetic sensitivity studies also show that reactions (2) and (3) are capable of regenerating flame radical species, thus countervailing reaction (1).[5]

Solid propellants which contain halogen components such as ammonium perchlorate also produce gaseous HCl as a major exhaust species. Gaseous HCl can intervene in the desired suppression chemistry by promoting formation of gaseous alkali chloride:

$$KOH \ (NaOH) + HCl \rightarrow KCl \ (NaCl) + H_2O \qquad (4)$$

$$KO_2 \ (NaO_2) + HCl \rightarrow KCl \ (NaCl) + HO_2 \qquad (5)$$
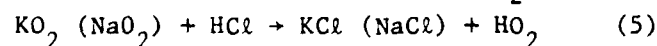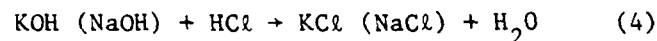
A thorough knowledge of the kinetic rate parameters of reactions 1-5 is required for accurate computer modeling of the effects of alkali afterburning

suppression as a function of propellant formulation and gun or rocket operating parameters. Without such models, propellant formulators have a difficult time determining the proper trade-off between the desirable secondary combustion suppression and the undesirable reduced primary combustion and enhanced corrosion effects imparted by alkali salt propellant additives.

The work presented in this report represents advanced experimental efforts to develop the capability to directly measure the required gas phase reaction rate parameters for refractory molecular species such as KOH, NaOH, KO_2 and NaO_2. Prior to this work, direct, gas phase, kinetic measurements involving these species were largely non-existent.

In order to perform these direct kinetic measurements, two preliminary problems had to be solved: first, reliable gas phase sources for the relevant alkali species K, Na, KOH, NaOH, KO_2 and NaO_2 had to be developed; second, reliable and sensitive ways to detect these species also had to be perfected. Only after the successful development of both generation and detection techniques for these refractory species could specific reaction rate parameters be determined.

The following sections of this report will present the development of both the gaseous alkali sources and detection techniques as well as the results of specific reaction rate parameter measurements.

2. Summary of Most Important Results

2.1 Development of Sources for Alkali Oxide and Hydroxide Species

Since the determination of reaction rate constants in the laboratory depends on the ability to create clean and well defined sources of the reactants, considerable effort was expended in the development of sources for K, Na, KO_2, NaO_2, KOH and NaOH which are suitable for flow reactor kinetic studies. Although the alkali species K and Na are relatively straight-forward to produce from vaporization of the solid, the oxide and hydroxide species are not readily produced by direct vaporization. The low vapor pressures of the solid alkali hydroxides combined with their chemical corrosiveness and tendency to form dimers makes direct vaporization unsuitable as a reactant source. We therefore explored gas phase chemical reactions whereby the easily vaporized Na or K could be converted quantitively and cleanly into the corresponding oxide or hydroxide.

NaO_2 and KO_2 may be formed by the direct recombination of the alkali atom with molecular oxygen

$$K \ (Na) + O_2 + M \rightarrow KO_2 \ (NaO_2) + M \ . \qquad (2)$$
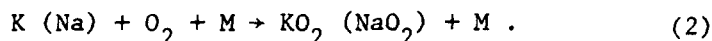
These reactions are relatively rapid compared to other three body processes and proceed with rate constants greater than $10^{-30} \ cm^6 s^{-1}$ at 300 K as determined in one of our publications from this work.[6] They can be used as a clean source of superoxide in flow reactors by prereacting the alkali atom with O_2 in a separate region with higher O_2 concentration to drive the reaction to completion before the products enter the main flow tube.

An alternative method for NaO_2 formation is the combination of bimolecular reactions of Na with ozone

$$Na + O_3 \ \rightarrow NaO + O_2 \qquad (6)$$

$$NaO + O_3 \rightarrow NaO_2 + O_2 \qquad (7a)$$

$$\rightarrow Na + 2O_2 \qquad (7b)$$

These reactions have been studied recently at Aerodyne[7] and are found to be rapid with $k_6 = 3.2 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$, $k_7 \sim 10^{-10} \text{ cm}^3\text{s}^{-1}$ and $k_{7a}/k_{7b} \sim 3$. Although some Na is initially reformed in Reaction 7b, the larger branching ratio for NaO_2 formation in 7a eventually dominates so that all Na will be converted to NaO_2. This bimolecular source of NaO_2 may be superior to the O_2 recombination source in experiments where the presence of minimal amounts of O_2 are desirable.

NaOH may be formed cleanly and quantitatively by reaction of Na with hydrogen peroxide

$$Na + H_2O_2 \rightarrow NaOH + OH \qquad (8a)$$
$$\rightarrow NaO + H_2O \qquad (8b)$$

Our measurements[8] of this reaction rate constant and branching ratio give values $k_{8a} = 4.2 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$ and $k_{8b} = 2.7 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$. Although Reaction 8 gives a mixture of NaOH and NaO, a pure source of NaOH may be produced by adding CO. This converts NaO back to Na via the reaction

$$NaO + CO \rightarrow Na + CO_2 \qquad (9)$$

After several cycles through Reactions 8 and 9 all the initial Na is converted to NaOH. This source and its application to the reaction of NaOH with HCℓ is described in detail in Reference 8.

The analogous reaction for K with H_2O_2 was also studied under this program. In this case, however, the channel forming KOH is considerably less than the KO channel,

$$K + H_2O_2 \rightarrow KOH + OH \qquad (10a)$$
$$\rightarrow KO + H_2O . \qquad (10b)$$

Attempts to observe KOH directly by observation with tunable diode laser absorption and indirectly by conversion back to K with atomic hydrogen, as was done successfully in the NaOH studies, indicated no detectable reaction for 10a. Attempts to detect the OH product using laser induced fluorescence also indicated no reaction although the analogous experiment in the Na case under the same experimental conditions did produce quantitative amounts of OH from reaction 8a. From the ratio of our OH detection limit and a quantitative measure of the initial K-atom concentration we obtain an upper limit to the branching ratio $k_{10a}/k_{10b} < 2 \times 10^{-3}$. The overall reaction rate for k_{10} was determined from the disappearance of K in excess H_2O_2 to be $k_{10} = 1 \times 10^{-11}$ $cm^3 s^{-1}$ which is somewhat slower than the analogous Na reaction.

2.2 Detection Methods For Gas Phase Alkali Species

Although atomic K and Na are readily detectable in the gas phase using laser induced fluorescence (LIF), the alkali oxides and hydroxides are much more difficult to detect sensitively and specifically. Since detection of these species is an important component for laboratory kinetic studies and eventually for in situ detection in combustion and atmospheric environments, we have made the development of detection methods a major emphasis of this program. These methods may be divided into two categories: (1) chemical conversion of the alkali oxide or hydroxide into the readily detectable Na or K atomic species and (2) direct spectroscopic methods using high resolution infrared absorption. The chemical conversion method has been used for NaOH and NaO in our published studies from this program.[8] The direct spectroscopic detection of KOH using infrared tunable diode laser absorption has also been accomplished under this program as described below. High resolution infrared absorption shows particular promise for the detection of other alkali species and is presently under further development at Aerodyne with Department of Energy sponsorship. More details on this method and sensitivity estimates for both sodium and potassium compounds are given in the Appendix.

2-3

Detection of NaOH and NaO by chemical conversion to Na is accomplished by addition of excess atomic hydrogen in the detection region just upstream of the LIF probe:

$$NaOH + H \rightarrow Na + H_2O \qquad (11)$$
$$NaO + H \rightarrow Na + OH \qquad (12)$$

The rate constant for reaction 11 has been determined in this study[8] to be $k_{11} > 4 \times 10^{-12} \, cm^3 s^{-1}$. Although H-atom addition and subsequent Na detection by LIF would not distinguish between NaOH and NaO, the latter may be detected independently by adding CO to the detection region which converts NaO to Na via reaction 9. No reaction was observed between NaOH and CO so that alternate additions of H and CO could be used to specifically detect either alkali species.

The main advantage of the chemical conversion of molecular alkali species to the corresponding atomic species is the extreme sensitivity of LIF detection for Na and K. Detection limits of less than 10^5 atoms cm^{-3} are achievable due to the high oscillator strengths of the D-line transitions.

Direct detection by high resolution infrared absorption is a more selective but less sensitive method for detecting molecular alkali species. We have applied this method to the detection of KOH in this program and report here the first observation of gas phase KOH using tunable diode laser absorption.

In these preliminary diagnostic studies, KOH was formed by vaporization of the solid in a 1 m long, 2 cm diameter, alumina tube which was heated in a muffle furnace to 1000 K. Solid KOH pellets were placed in a silver boat inside the tube to prevent corrosion. The diode laser beam passed through the center of the tube and was collected on a copper doped germanium detector. The laser was tuned to cover the frequency region from 424.1 to 424.5 cm^{-1} which was calculated to be close to the peak of the R-branch of the K-OH stretch band. The low resolution infrared data of Spinar and Margrave[9] was combined with rotational constants obtained from microwave spectra[10,11] to calculate the positions of the strongest lines.

2-4

Typical spectra are shown in Figure 1 where the increase in KOH concentration as a function of oven temperature is apparent. The 945 K spectrum shows one strong line and several weaker transitions due to hot bands. The ratio of hot band lines to the fundamental band line increases rapidly with temperature from 945 to 1030 K as expected from the partition functions for these low energy combination bands.[11] The appearance of numerous hot bands and the limited signal to noise in these initial experiments has prevented a thorough analysis of these spectra. A low temperature KOH source would greatly simplify the spectrum.

HEATER
TEMPERATURE

870 K

945 K

1030 K

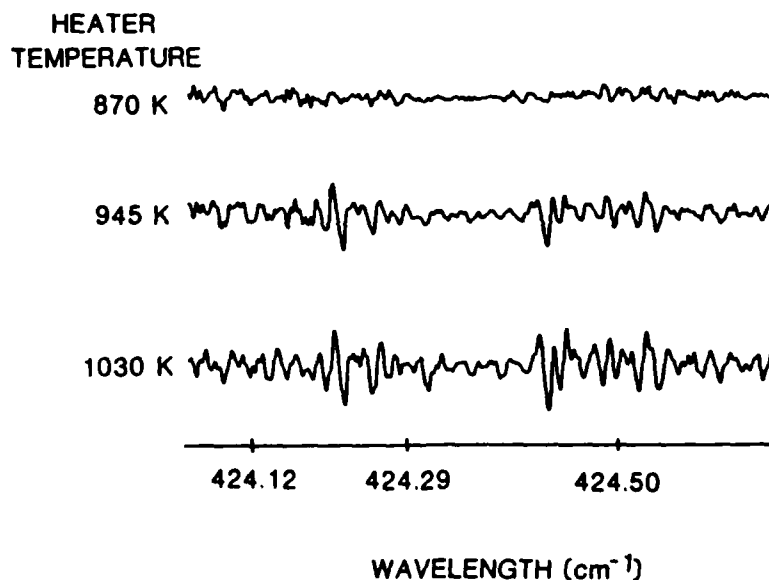424.12   424.29   424.50

WAVELENGTH (cm⁻¹)

Figure 1.   Absorption Spectra of KOH in Second Derivative Mode.
The maximum absorption is approximately 2%.

This initial result demonstrates a potentially powerful diagnostic for gas phase molecular alkali species which will be valuable for both laboratory kinetic studies and even for field measurements under combustion conditions at atmospheric pressure. This diagnostic method is universally applicable to a number of alkali species of interest including KOH, NaOH, KO, NaO, KO_2, NaO_2, KCℓ and NaCℓ. Estimates on the line strengths and detection sensitivities and a more general description of the diode laser absorption method is given in the Appendix.

2.3 Kinetic Studies of Alkali Species

The sources and detection methods described above have been employed in the study of a number of reactions during the course of this program. Reaction rate constants and product branching ratios have been determined using a high temperature fast flow reactor which can operate over the range 300 to 1300 K. The apparatus and methods used have been described in previous publications.[12,13] The specific applications to alkali chemistry are described in detail in the publications resulting from this contract.[6,8] The reactions studied and the measured rate constants are summarized in Table 1.

The recombination reactions of Na and K with O_2

$$K \ (Na) + O_2 + M \rightarrow KO_2 \ (NaO_2) + M \tag{2}$$
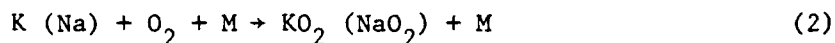
have been studied over the temperature range 300 to 700 K and with M = N_2, He and Ar. The resulting rate constants (Table 1) are greater than those deduced from earlier flame studies of Carabetta and Kaskan[14] which were the only ones available for flame suppression modeling at the beginning of this program. Several other studies[15-17] have since confirmed this faster rate and it is now well established that these reactions are sufficiently rapid to be important in combustion and alkali flame suppression chemistry.

Measurements of the reaction of sodium hydroxide with atomic hydrogen

$$NaOH + H \rightarrow Na + H_2O \tag{1}$$

Table 1. Summary of Measured Reaction Rate Constants for Alkali Species

Reaction	T(K)	Rate Constant
$K + O_2 + N_2 \rightarrow KO_2 + N_2$	302-720	$(5.4 \pm 0.2) \times 10^{-30}(T/300)^{-0.56 \pm 0.20}$ $cm^6 s^{-1}$
$K + O_2 + He \rightarrow KO_2 + He$	296-520	$(2.0 \pm 0.5) \times 10^{-30}(T/300)^{-0.9 \pm 0.5}$ $cm^6 s^{-1}$
$K + O_2 + Ar \rightarrow KO_2 + Ar$	300	$(3.5 \pm 1) \times 10^{-30}$ $cm^6 s^{-1}$
$Na + O_2 + N_2 \rightarrow NaO_2 + N_2$	320-700	$(1.9 \pm 0.4) \times 10^{-30}(T/300)^{-1.1 \pm 0.5}$ $cm^6 s^{-1}$
$Na + O_2 + He \rightarrow NaO_2 + He$	310-470	$(1.4 \pm 0.3) \times 10^{-30}(T/300)^{-0.9 \pm 0.5}$ $cm^6 s^{-1}$
$Na + O_2 + Ar \rightarrow NaO_2 + Ar$	324	$(1.2 \pm 0.3) \times 10^{-30}$ $cm^6 s^{-1}$
$Na + H_2O_2 \nearrow NaOH + OH$	308	$(4.1 \pm 1.8) \times 10^{-11}$ $cm^3 s^{-1}$
$\searrow NaO + H_2O$		$(2.8 \pm 1.2) \times 10^{-11}$ $cm^3 s^{-1}$
$K + H_2O_2 \nearrow KOH + OH$	300	$< 2 \times 10^{-14}$ $cm^3 s^{-1}$
$\searrow KO + H_2O$		$(1.0 \pm 0.5) \times 10^{-11}$ $cm^3 s^{-1}$
$K + H_2O \rightarrow KOH + H$	1273	$< 3 \times 10^{-15}$ $cm^3 s^{-1}$
$NaOH + H \rightarrow Na + H_2O$	300	$> 4 \times 10^{-12}$ $cm^3 s^{-1}$
$NaOH + HCl \rightarrow NaCl + H_2O$	300	$(2.8 \pm 0.9) \times 10^{-10}$ $cm^3 s^{-1}$
$NaO + HCl \rightarrow NaCl + OH$	300	2.8×10^{-10} $cm^3 s^{-1}$
$NaCl + H \rightarrow Na + HCl$	300	5×10^{-14} $cm^3 s^{-1}$
$NaO_2 + HCl \rightarrow NaCl + HO_2$	300	$(2.3 \pm 0.4) \times 10^{-10}$ $cm^3 s^{-1}$

indicate that this reaction is rapid with a rate constant greater than 4×10^{-12} cm^3s^{-1} at 300 K. This is an important result for flame suppression modeling since this reaction is believed to be the main radical scavenging mechanism in alkali-seeded flames. Our result for this rate constant is considerably greater than that extrapolated from the flame data by Jensen and Jones[18] who obtain a value of 1.8×10^{-11} $e^{-990/T}$ or 6.6×10^{-13} cm^3s^{-1} at 300 K.

The rate constant for the analogous reaction of potassium hydroxide with atomic hydrogen

$$KOH + H \rightarrow K + H_2O \qquad (1)$$
$$\leftarrow \qquad (-1)$$

has not yet been determined, although significant progress towards this goal was made during this contract. Direct detection methods for both KOH, using infrared diode laser absorption, and for H-atoms, using resonance fluorescence at 121.6 nm, have been implemented on our flow tube. The rate measurement, however, has been hindered by the lack of a suitable source of gas phase KOH. The reaction of K with hydrogen peroxide

$$K + H_2O_2 \rightarrow KOH + OH \qquad (10a)$$
$$\rightarrow KO + H_2O \qquad (10b)$$

was found to yield mostly KO rather than KOH with $k_{10a}/k_{10b} < 2 \times 10^{-3}$. The analogous Na reaction yielded nearly 60% NaOH. The other source of KOH which was tried, high temperature sublimation of solid KOH, also proved unsuitable as a flow tube source due to its highly corrosive nature and its tendency to form KOH dimers. A more suitable source of gas phase KOH needs to be developed before this reaction rate can be directly determined.

An attempt to determine the rate of KOH + H through measurement of the rate constant for the reverse reactions

$$K + H_2O \rightarrow KOH + H \qquad (11)$$

also proved unsuccessful. In this experiment the resonance fluorescence signal for atomic potassium was monitored as water vapor was added to the flow reactor. Experiments at temperatures of 973, 1173 and 1273 K showed no detectable reaction which establishes an upper limit for this rate constant of $k_{-1} < 3.6 \times 10^{-15}$ cm^{3}s^{-1}. In theory an upper limit for k_1 may be established by combining k_{-1} with the thermodynamic equilibrium constant
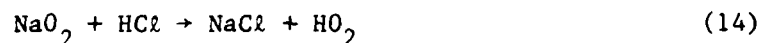
$$K_{eq} = k_1/k_{-1}.$$

In this case, combining our upper limit for k_{-1} with K_{eq} implies only that $k_1 < 2 \times 10^{-10}$ cm^{3}s^{-1}. A lower measurable limit for k_{-1} or a higher experimental temperature is required to set a more meaningful upper limit for k_1. Attempts to extend the experimental temperature range to 1500 K, however, were thwarted by the large K background fluorescence from the hot flow tube walls which prevented meaningful measurements of the decay rate of K with H_2O at these temperatures.
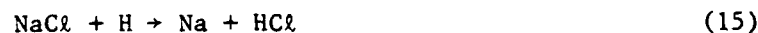
The reaction of gas phase NaOH with HCl[8]

$$NaOH + HCl \rightarrow NaCl + H_2O \tag{4}$$
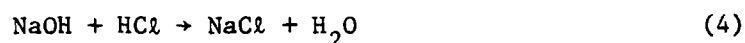
was found to procede essentially at its gas kinetic limit with a rate constant of 2.8×10^{-10} cm^{3}s^{-1} at 308 K. This reaction could be an important process in flame suppression chemistry of fuels such as perchlorates with a high halogen content. The reaction may also be important in upper atmospheric chemistry of meteor-ablated sodium and was measured in conjunction with other programs to study the effects of alkali chemistry on stratospheric ozone. Other reactions studied during this program[8,19] include

$$NaO + HCl \rightarrow NaC + OH \tag{13}$$
$$NaO_2 + HCl \rightarrow NaCl + HO_2 \tag{14}$$
and
$$NaCl + H \rightarrow Na + HCl \tag{15}$$

which could also participate in perchlorate fuel flame suppression chemistry.

Both the NaO + HCl and NaO$_2$ + HCl reactions were found to procede at their gas kinetic limits with k_{13} = 2.8 x 10^{-10} cm^{3}s^{-1} and k_{14} = 2.3 x 10^{-10} cm^{3}s^{-1} at 300 K.[19] Since these bimolecular reactions are already in their gas kinetic limits and since they procede via an electron jump mechanism, no large temperature dependence is expected and these rate constants should also be applicable to combustion temperatures. The NaCl + H reaction is much slower with $k_{15} \sim$ 5 x 10^{-14} cm^{3}s^{-1}. The successful measurements of these reaction rate constants vividly demonstrates the versatility of the fast flow reactor technique for further kinetic studies of alkali oxide and hydroxide species.

3. List of Publications

1. J. A. Silver, M. S. Zahniser, A. C. Stanton, and C. E. Kolb, "Temperature Dependent Termolecular Reaction Rate Constants for Potassium and Sodium Superoxide Formation", Twentieth Symp. (International) on Combustion, The Combustion Institute, 1984, pp 605-612.

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4. List of Scientific Personnel

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APPENDIX

Tunable Diode Laser Detection of Molecular Alkali Species

Overview

Most heteronuclear molecular species in the gas phase can in principle be detected optically by measurement of absorption by their characteristic vibrational-rotational transitions. Very sensitive detection is possible by the use of cryogenically cooled detectors and bright, nearly monochromatic light sources, e.g., tunable diode lasers. Aerodyne personnel have substantial experience and several currently active programs in the detection of a wide range of stable and transient species by tunable diode laser absorption. We have assessed the applicability of this technique to the detection of molecular alkali species under combustion conditions and have concluded that the technique offers considerable promise for the selective in situ detection of these gas phase species with sensitivities of better than 10 ppm. The application of this method to low pressure flow reactors for alkali reaction rate studies will be more sensitive and allow detection limits on the order of 10^{10} to 10^{11} molecules cm^{-3}. In the following subsections, we provide a description of the tunable diode laser detection apparatus and methodology, and estimate the detection sensitivities for several alkali compounds by this technique.

Tunable Diode Laser Apparatus and Methodology

The instrumentation for a tunable diode laser diagnostic is shown in Figure A1. The diode laser itself is housed in a temperature-controlled closed cycle refrigerator. This system is a commercial system from Spectra-Physics (Laser Analytics Division). An off-axis paraboloidal reflector is used to collect and collimate the multimode laser emission. This emission is mechanically chopped and refocused at the entrance slit of a 0.25 meter monochromator, equipped with a 30 groove/mm grating brazed for 25 μm. The single laser mode selected by the monochromator is then transmitted by additional reflective optics through the multi-pass analysis region and ultimately to a cryogenically cooled infrared detector. A fraction of the laser beam intensity is split off prior to entering the analysis region and is focused on a second detector. This dual beam (analysis beam and reference beam) arrangement permits the direct measurement of fractional absorption in the analysis region as the laser is tuned across a molecular absorption feature. The amplified signals from the detectors are fed to lock-in amplifiers for synchronous measurement. The lock-in amplifier outputs are digitized with a simultaneous sample and hold A/D system and the data are transferred to a microcomputer (IBM Personal Computer XT, DMA interface) for ratioing, analysis, and graphical display.

The multipass cell allows as many as 100 or more optical passes through the analysis region. A practical limit to the useful number of passes is set by mirror reflectivity losses which ultimately reduce signal-to-noise.
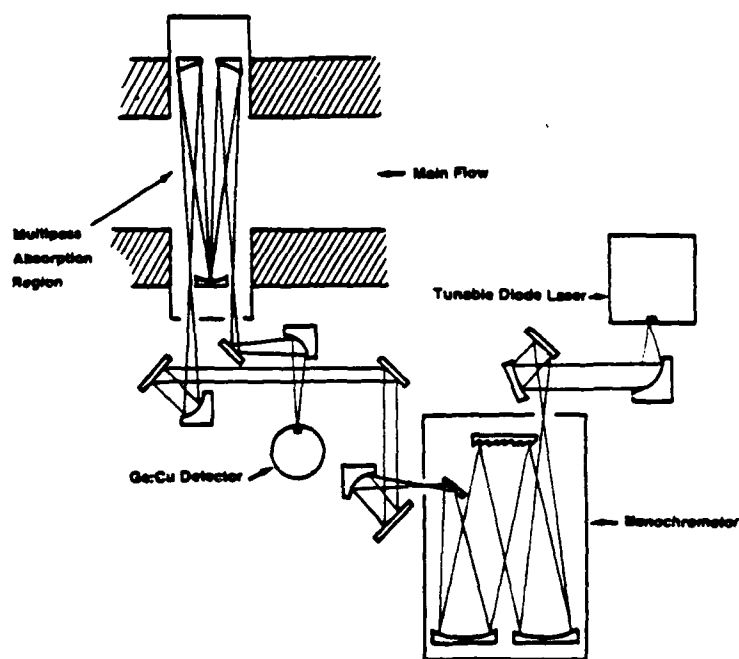
Figure A1. Typical Setup for IR Diode Laser Absorption Experiments

Our previous experience suggests that 40 passes is optimum. For the approximately 10 cm flow width of the flow tube, the total multiple pass path length (40 passes) is approximately 4 meters.

High resolution tuning (laser linewidth $\simeq 10^{-4}$ cm^{-1}) of the laser wavelength is accomplished by variation of the laser current. A typical laser mode of the recently introduced stripe geometry diode lasers has a current tuning range of $\sim$ 2 cm^{-1}. Atmospheric pressure absorption lines have linewidths (full width at half maximum) of approximately 0.1 cm^{-1}. Thus the laser will easily tune across the full width of these broad absorption lines with complete resolution of the absorption profile. Wavelength calibration of the lasers is accomplished by measurement of the low pressure absorption spectrum of a well-characterized calibration gas. For measurements in the 350 to 450 cm^{-1} region, where many of the molecular alkali species have absorption bands, the CS_2 band provides a rich source of calibration lines.[1]

Estimated Detection Sensitivities

The sensitivity for detection of a given species by tunable diode laser absorption depends essentially on two factors: the minimum fractional absorption measurable by the instrumentation, and molecular parameters which

A-2

determine the absorption strength corresponding to a given species con-
centration. We briefly examine these issues in this subsection and provide
estimates for the detection sensitivities for several molecular alkali species.

Tunable diode laser systems are capable of very high sensitivity for
measurement of small fractional absorptions. This high sensitivity derives
from the brightness of the laser (typically 0.01 - 0.1 mW single mode source
power), high detectivity of the cryogenically cooled detectors ($D* > 10^{10}$ cm
$Hz^{0.5}$ W^{-1}), and exceptionally low amplitude noise of the lasers (often
detector-limited). In our experience, fractional absorptions as low as 0.01%
can be detected routinely with these lasers for low pressure absorption lines,
and detection of 0.001% absorption has been reported (e.g., Ref. 2) even for
lines at atmospheric pressure. Detection of these broad lines (0.1 cm^{-1}) is
nonetheless more difficult than measurement of low pressure lines, because
substantial variation of the laser baseline intensity normally occurs over the
absorption linewidth and accurate measurement of this slow variation is
difficult even with a dual-beam system. In addition, turbulence at atmospheric
pressures imposes an additional noise source on the probe beam and may result
in degraded sensitivity. In consideration of these factors, we adopt 0.1%
fractional absorption as a conservative estimate of the detection sensitivity
of the instrumentation for measurement of pressure-broadened lines. We
emphasize, however, that an improvement by 1 to 2 orders of magnitude in this
sensitivity may be possible.

The absorption strength for molecular absorption lines may be calculated
if the vibrational band strength (the integrated absorption strength of the
band) is known. In general, this parameter is not known for the alkali
species, however estimates are possible based on simple models of the bonding
in these molecules. The parameter of interest is the dipole moment derivative
along the bond axis, evaluated at the equilibrium atomic separation. The
vibrational band strength, in units of cm^{-2} (STP atm)$^{-1}$ is then[3]

$$S_{band} = \frac{188}{M_r} \left| \frac{d\mu}{dR} \right|^2_{R_e} \quad , \qquad (1)$$

where M_r is the reduced mass in a.m.u. and $(d\mu/dR)_{R_e}$ is the dipole moment
derivative in debye $\overset{\circ}{A}^{-1}$.

The simple model which we adopt to describe bonding in the alkali halides,
hydroxides, and monoxides is the "Rittner Model".[4] In this model, the molecule
is pictured as being constituted of a positive and negative ion, each of which
is polarized by the electrostatic field of the other. Expressions for the
dipole moment and dipole moment derivative may then be derived on the basis of
classical theory, depending only on the ion polarizabilities.

For the dipole moment derivative, the resulting expressions is[5]

$$\frac{d\mu}{dR}\bigg|_{R_e} = 3e - \frac{2\mu}{R_e} \quad , \qquad (2)$$

where e (4.8 debye $\overset{o}{A}^{-1}$) is the electronic charge. Equations (1) and (2) may then be used as a basis for estimating the band strengths.

The estimated band strengths for several molecular alkali species are given in Table A1.

Table A1 - Estimated Dipole Moment Derivatives (Rittner Model) and Infrared Vibrational Band Strengths for Selected Alkali Halide, Hydroxide, and Monoxide Species[a]

Species	ν_o (cm^{-1})	R_e (Å)	μ_e(debye)	$\frac{d\mu}{dR}\big\|_{Re}$ (debye/Å)	S_{Band} (cm^{-2} STP atm^{-1})
^{7}LiF	894.0	1.5639	6.2839	6.4 7.94[b]	1500 2600[b]
NaF	528.4	1.9259	8.1234	6.0	650
Na^{35}Cl	361.1	2.3609	8.9721	6.8	630
NaOH[c]	431[7]	1.95[8]	6.9[d]	7.9	1200
NaO	526[9]	2.05[9]	9.8[e]	4.8	460
KF	421.393[10]	2.1715	8.5583	6.5	620
K^{35}Cl	277.5	2.6668	10.2384	6.7	460
KOH[c]	408[11]	2.2115[12]	7.7[d]	7.4	870
KO	384[9]	2.22[9]	10.7[e]	4.8	380

[a] Unless otherwise indicated, experimental values for $\nu_o = \omega_e - 2\omega_e x_e$, R_e, and μ_e are abstracted from the summary of data given in Brumer and Karplus.[6]

[b] Obtained from experimental measurement of the v = 1 radiative lifetime for ^{6}LiF using an electric-resonance molecular beam technique.[5]

[c] M-OH bonds

[d] Calculated dipole moments obtained from the Rittner model.[13] For most alkali halides, the Rittner model underpredicts the dipole moment (as compared with experimental values) by 5% to 15%.[6]

[e] Estimated as the point charge dipole moment, $\mu_{pc} = eR_e$. The tendency of this model is to overpredict the dipole moment for the alkali halides by 20% to 30%.[6]

For the alkali halides, accurate experimental values are available for R_e and the dipole moment, μ. These values are used in Eq. (2) whenever possible. To our knowledge only one direct comparison to an experimental value for the dipole moment derivative is available for the species in our table, i.e., for LiF. For LiF, the measured derivative (and therefore the band strength) are actually larger than the values predicted by the simple theory. Interestingly, a much more rigorous quantum mechanical calculation of the dipole moment derivative for LiF[14] produces much poorer agreement with the experimental value than does the simple Rittner model.

The band strengths for these species as estimated in Table Al are quite strong, although not out of line with the vibrational band strengths for more familiar species. For example, the measured values of S_{band} for CO and CO_2 (asymmetric stretch) are 250 cm^{-2} (STP atm)$^{-1}$ [15] and 2680 cm^{-2} (STP atm)$^{-1}$,[16] respectively. Experimental evidence that these alkali species can be measured by infrared absorption in the gas phase comes from the studies of Spinar and Margrave[17] and the recent diode laser measurements of Maki and Lovas[10]. Spinar and Margrave observed the broad band gas phase absorption spectra of LiOH, NaOH, and KOH using a low resolution infrared spectrometer. Although the conditions of their experiments are not well documented, their data suggest the absorption measurement of $\sim$ 10 ppm NaOH over a 50 cm path using this relatively insensitive broadband technique. More recently, Maki and Lovas had little difficulty in measuring the first overtone spectrum of gas phase KF with a tunable diode laser[10] over a 36 cm path length. The fundamental band indicated in Table Al should be substantially stronger than the overtone bands which Maki and Lovas measured.

From the estimated band strengths, the absorption cross section at line center of individual lines can be obtained, and estimates of the detection sensitivity follow directly. The line strength (cm^2 molecule^{-1} cm^{-1}) for these simple diatomic and linear triatomic molecules, at temperature T is

$$S_J = \frac{S_{band}}{N_o} \frac{\nu_J}{\nu_o} (1 - e^{-\nu_o h c/kT}) \frac{hcB}{kT} (2J+1)e^{-BJ(J+1)hc/kT} , \qquad (3)$$

where J is the rotational quantum number of the lower level in the transition, B is the rotational constant, N_o is Loschmidt's number (2.69 x 10^{19} molecules cm^{-3}), and ν_J is the frequency of the particular P or R branch line originating from J. The line center absorption cross section for an atmospheric pressure-broadened line can be estimated as

$$\sigma_o \approx \frac{S_J}{0.1} \; cm^2 \; molecule^{-1} \qquad , \qquad (4)$$

where 0.1 cm^{-1} is the approximate linewdith at atmospheric pressure. Finally, the minimum detectable concentration n_{min}(cm^{-3}) may be estimated from

$$\left(\frac{\Delta I}{I_o}\right)_{min} \approx n_{min} \, \sigma_o \ell = 0.001 \tag{5}$$

or

$$n_{min} = \frac{0.001}{400 \, \sigma_o} \quad , \tag{6}$$

where we assume an absorption path length ℓ of 400 cm and a minimum detectable fractional absorption of 0.1%. At elevated temperatures, excited vibrational levels ($v > 0$) become significantly populated in many cases, which means that n_{min} should be replaced in Eqs. 5 and 6 with $(n_{lower} - n_{upper})_{min}$. These population differences can be calculated from thermal Boltzmann distributions and related to the total number density of the species. The overall effect of this is to degrade the minimum detectable concentration.

The estimated line center absorption cross sections and minimum detectable concentrations (including vibrational partitioning) for several molecular alkali species at T = 1200 K are given in Table A2, based on Eqs. (3) - (6) and the band strength estimates of Table A1. In addition, we include estimates for KO_2 and NaO_2 detection in the 400 cm^{-1} region, assuming similar band strengths as the corresponding monoxide species. Potassium chloride is not included in the table because the vibrational frequency for KCl (~ 278 cm^{-1}) is outside the wavelength range of commercial diode lasers. The strongest IR-active bands of the alkali sulfate species, measured in argon or nitrogen matrices, are in the 1100 cm^{-1} region.[18] Measurement of these latter two species may be more difficult, however, because virtually nothing is known about the spectroscopy and also the vibrational bands are likely to be weak compared with the bands of smaller molecules.

The sensitivity estimates shown in the table indicate that concentrations of a few ppm of the various chloride, hydroxide, and oxide species should be readily measurable by diode laser absorption for combustor test conditions. We reemphasize that even greater sensitivity (detection of less than 0.1% absorption) should be possible with appropriate attention to the instrumentation. Also, the technique is attractive in that only one or two diode lasers would be required to cover the wavelength tuning range needed for measurement of these species ($\sim 350 - 550$ cm^{-1}).

Table A2 - Estimated Line Center Absorption Cross Sections and Minimum
Detectable Concentrations at T = 1200 K, P = 1 atm, for
Tunable Diode Laser Measurement of Molecular Alkali Species
(Multiple Pass Path Length = 400 cm)

Species	σ_o (cm^2 molecule^{-1})	Detectable Concentration, cm^{-3}
NaOH	3.5×10^{-18}	2.4×10^{13} (3.9 ppm)
NaCl	1.1×10^{-18}	1.0×10^{13} (1.6 ppm)
NaO	1.5×10^{-18}	6.8×10^{12} (1.1 ppm)
NaO$_2$	(1.5×10^{-18})	5.7×10^{13} (9.3 ppm)
KOH	2.0×10^{-18}	4.4×10^{13} (7.2 ppm)
KO	8.2×10^{-19}	1.3×10^{13} (2.1 ppm)
KO$_2$	(8.2×10^{-19})	1.0×10^{14} (16 ppm)
Na$_2$SO$_4$	?	Probably > 10 ppm
K$_2$SO$_4$	?	Probably > 10 ppm

The sensitivity estimates in Table A2 are for atmospheric pressure
measurements for in situ alkali species detection under combustion conditions.
For applications to low pressure flow tube kinetic studies of alkali species
the detection limits will be considerably lowered due to the absence of line
broadening. At pressures less than 20 torr, the line widths are determined
mainly by their Doppler component which is typically two orders of magnitude
less than the collisional width at 760 torr. Since the line center absorption
increases proportionally, the detection limit for the same path length will
decrease by a factor of 100 from the values in Table A2. A further sensitivity
increase is obtained since fractional absorptions of 0.01% are readily detect-
able under controlled laboratory conditions. Thus the detection limits under
these conditions would be in the range 10^{10} to 10^{11} molecules cm^{-3}.

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