A Study of Atmospheric Reactions of Neutral Sodium Species and Other Metals of Meteoric Origin

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Abstract:
The reactions of metallic species introduced into the atmosphere by meteor ablation may play a significant role in the chemistry of the lower thermosphere and upper stratosphere. The work described in this report summarizes a series of experimental rate constant measurements for reactions pertinent to these atmospheric regions.

Prior to this work, virtually no direct kinetic parameters had been measured for the reactions of alkalis, and in particular sodium, which are believed to occur between 30 and 100 km in altitude. Model predictions of excited sodium emissions, expected concentration levels of the various alkali species, and the potential impact of alkali chemistry on the ozone balance all depended on theoretical estimates of reaction rate constants and product branching ratios.

Using a high temperature fast flow reactor and a variety of atomic and molecular species source and detection techniques, we have measured rate constants for over a dozen reactions.
The results of these measurements lead to the following conclusions:

a) Below 85 km, the prime reaction for removal of atomic sodium is the termolecular reaction with O₂ to form NaO₂, not the reaction with ozone as had been previously believed.

b) The major alkali species which leaves the mesosphere is most likely NaO₂ or NaOH, but not NaO.

c) In the upper stratosphere, it is possible that alkali reactions have a significant effect on the concentration of ozone. The reactions of NaO, NaOH, and NaO₂ with HCl are all very rapid, leading to the formation of NaCl, which subsequently photodissociates. The rates of these processes are such that sodium can act as a catalytic agent in the release of free chlorine, which then attacks ozone.

d) More detailed in situ atmospheric measurements of both atomic and molecular forms of sodium and other meteor metals should be performed.

e) Investigation of heterogeneous loss processes for gaseous meteor metals are recommended.
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EXECUTIVE SUMMARY

The reactions of metallic species introduced into the atmosphere by meteor ablation may play a significant role in the chemistry of the lower thermosphere and upper stratosphere. The work described in this report summarizes a series of experimental rate constant measurements for reactions pertinent to these atmospheric regions.

Prior to this work, virtually no direct kinetic parameters had been measured for the reactions of alkalis, and in particular sodium, which are believed to occur between 30 and 100 km in altitude. Model predictions of excited sodium emissions, expected concentration levels of the various alkali species, and the potential impact of alkali chemistry on the ozone balance all depended on theoretical estimates of reaction rate constants and product branching ratios.

Using a high temperature fast flow reactor and a variety of atomic and molecular species source and detection techniques, we have measured rate constants for over a dozen reactions. The results of these measurements lead to the following conclusions:

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e) Investigation of heterogeneous loss processes for gaseous meteor metals are recommended.
1. OBJECTIVE

1.1 Introduction

Metallic elements volatilized during meteor entry into the Earth's upper atmosphere play a significant role in the structure of the D and E regions of the ionosphere,\textsuperscript{1-2} and, at least in the case of sodium, the visible day and nightglow emissions from the mesosphere and lower thermosphere.\textsuperscript{3-5} Recently, it was suggested that sodium and other meteor metals may be important in stratospheric chemistry by affecting ozone reduction by the catalytic chlorine cycle.\textsuperscript{6-8}

The influx of meteor metals into the upper atmosphere has been estimated\textsuperscript{9} to be $3.5 \times 10^6$ kg yr$^{-1}$, with a sodium abundance of 2% leading to a calculated sodium flux of $1.2 \times 10^4$ atoms cm$^{-2}$ s$^{-1}$. Other estimates of sodium flux run as high as $2 \times 10^4$ cm$^{-2}$ s$^{-1}$.\textsuperscript{10} The flux of other metallic species such as Mg, Ca, Al, Si and Fe will be as much as 10 times higher and speculative concerns about their influence on upper atmospheric homogeneous and heterogeneous chemistry have been published.\textsuperscript{1-2,7-8,10}

Unfortunately, all attempts to model the role of volatilized meteor metals (particularly sodium) in the mesosphere and stratosphere\textsuperscript{3-4,7,9-15} have suffered from an almost total lack of measured rate constants. All such models start with the oxidation of sodium or other metallic species in reaction with atmospheric $O$, $O_2$, or $O_3$. Through 1982, the only measured chemical rate constants available for any meteor metal oxidation reactions were the three body recombination reactions of alkali atoms (Na, K) with $O_2$:\textsuperscript{16-18}

\begin{equation}
Na \text{ or } K + O_2 + M \rightarrow NaO_2 \text{ or } KO_2 + M.
\end{equation}

1-1
Flame studies by Hynes et al.\textsuperscript{19} and direct measurements at 724 and 844 K by Hussain and Plane\textsuperscript{18} showed that this reaction rate is 1000 times faster than previously believed.\textsuperscript{16–17} Recent direct flow tube measurements\textsuperscript{20} in our laboratory have extended these results from 700 K down to 300 K, and show that the reaction rates vary inversely with temperature, and confirm the larger values for the rate constants.

As an indication of the effect that the availability of chemical rate data has on aeronomic modeling studies, consider the theoretical calculation of several important sodium oxidation reaction rate constants:

\begin{equation}
\text{Na} + \text{O}_3 \rightarrow \text{NaO} + \text{O}_2 \quad (2)
\end{equation}

\begin{equation}
\text{NaO} + \text{O} \rightarrow \text{Na} + \text{O}_2 \quad (3)
\end{equation}

and

\begin{equation}
\text{NaO} + \text{O}_3 \rightarrow \text{Products} \quad (4)
\end{equation}

performed at Aerodyne Research, Inc.\textsuperscript{21} The adoption of realistic values for just these three rate constants has led to a major revision in the understanding of the structure of the mesospheric sodium layer,\textsuperscript{22} the magnitude of the sodium D line nightglow,\textsuperscript{5,21} and the understanding of long-lived luminous meteor trails.\textsuperscript{8,21}

From the recent modeling work\textsuperscript{7–8,10,13,21–22} and comparison of these models with atmospheric measurements,\textsuperscript{12,14–15} neutral sodium is believed to be transformed via a series of chemical reactions involving NaO, NaO\textsubscript{2}, and NaOH. A survey of the relevant literature\textsuperscript{6–8,10,13} provides a fairly complete list of possible neutral sodium reactions of importance. These are listed in Table 1, in four groups, which to some extent, reflect the sequence of events from the introduction of neutral sodium at 110 km altitude to its disappearance near 70 km. Also listed are reaction enthalpies, with associated uncertainties.
Table 1 - Atmospheric Reactions of Neutral Sodium Species

<table>
<thead>
<tr>
<th>I. Sodium Atom Reactions</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>$\text{Na} + \text{O}_2 \rightarrow \text{NaO}_2$</td>
<td>163 ±21</td>
</tr>
<tr>
<td>$\text{Na} + \text{O}_3 \rightarrow \text{NaO} + \text{O}_2$</td>
<td>167 ±42</td>
</tr>
<tr>
<td>$\text{Na} + \text{HO}_2 \rightarrow \text{NaOH} + \text{O}$</td>
<td>77 ±15</td>
</tr>
<tr>
<td>$\text{NaH} + \text{O}_2$</td>
<td>4 ±21</td>
</tr>
<tr>
<td>$\text{NaO} + \text{OH}$</td>
<td></td>
</tr>
<tr>
<td>$\text{Na} + \text{O} \rightarrow \text{NaO}$</td>
<td>273 ±42</td>
</tr>
</tbody>
</table>

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<tr>
<th>II. Sodium Oxide Reactions</th>
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</thead>
<tbody>
<tr>
<td>$\text{NaO} + \text{O}_3 \rightarrow \text{NaO}_2 + \text{O}_2$</td>
</tr>
<tr>
<td>$\text{NaO} + \text{H}_2\text{C} \rightarrow \text{NaOH} + \text{OH}$</td>
</tr>
<tr>
<td>$\text{NaO} + \text{H}_2 \rightarrow \text{NaOH} + \text{H}$</td>
</tr>
<tr>
<td>$\text{NaO} + \text{CH}_4 \rightarrow \text{NaOH} + \text{CH}_3$</td>
</tr>
<tr>
<td>$\text{NaO} + \text{HCl} \rightarrow \text{NaCl} + \text{OH}$</td>
</tr>
<tr>
<td>$\text{NaO} + \text{O} \rightarrow \text{Na} + \text{O}_2$</td>
</tr>
<tr>
<td>$\text{NaO} + \text{HO}_2 \rightarrow \text{NaOH} + \text{O}_2$</td>
</tr>
<tr>
<td>$\text{NaO} + \text{H} \rightarrow \text{NaOH}$</td>
</tr>
<tr>
<td>$\text{NaO} + \text{CO} \rightarrow \text{NaOCl} + \text{O}$</td>
</tr>
<tr>
<td>$\text{NaO}_2 + \text{HCl} \rightarrow \text{NaCl} + \text{HO}_2$</td>
</tr>
<tr>
<td>$\text{NaO}_2 + \text{Cl} \rightarrow \text{NaCl} + \text{O}_2$</td>
</tr>
<tr>
<td>$\text{NaO}_2 + \text{CO} \rightarrow \text{NaCl} + \text{O}_3$</td>
</tr>
<tr>
<td>$\text{NaO}_2 + \text{H}_2 \rightarrow \text{NaOH} + \text{OH}$</td>
</tr>
<tr>
<td>$\text{NaO}_2 + \text{H}_2 \rightarrow \text{NaOH} + \text{O}_2$</td>
</tr>
<tr>
<td>$\text{NaO}_2 + \text{H} \rightarrow \text{NaOH} + \text{O}$</td>
</tr>
<tr>
<td>$\text{NaO}_2 + \text{H} \rightarrow \text{NaOH} + \text{OH}$</td>
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<tr>
<th>III. Sodium Hydroxide Reactions</th>
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<tr>
<td>$\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{NaOH} + \text{Cl} \rightarrow \text{NaCl} + \text{OH}$</td>
</tr>
<tr>
<td>$\text{NaOH} + \text{CO}_2 \rightarrow \text{NaHCO}_3$</td>
</tr>
<tr>
<td>$\text{NaOH} + \text{HNO}_3 \rightarrow \text{NaNO}_3 + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{Products}$</td>
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</tbody>
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<th>IV. Photolysis Reactions</th>
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<tr>
<td>$\text{NaOH} + \text{hv} \rightarrow \text{Na} + \text{OH}$</td>
</tr>
<tr>
<td>$\text{NaO} + \text{hv} \rightarrow \text{Na} + \text{O}_2$</td>
</tr>
<tr>
<td>$\text{NaO}_2 + \text{hv} \rightarrow \text{Na} + \text{O}_3$</td>
</tr>
<tr>
<td>$\text{NaCl} + \text{hv} \rightarrow \text{Na} + \text{Cl}$</td>
</tr>
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</table>
The main removal mechanisms of sodium are by reaction with $O_2$ or $O_3$, the latter reaction used by Chapman\textsuperscript{23} to describe the Na nightglow. The recent rate measurements of reaction (1) however, lead us to believe that below 80 km most of the Na is converted to NaO$_2$.

The fate of NaO$_2$, however, is uncertain. Recent measurements by Figger et al\textsuperscript{24} and flame studies by Hynes et al\textsuperscript{19} imply that the Na-O$_2$ bond strength is much weaker than previously believed, with a value of ca. 163 kJ mol$^{-1}$. As a result, NaO$_2$ will react exothermically with atomic oxygen to produce NaO. Sodium oxide can react either with ozone to reform NaO$_2$ or Na, or react with water to produce NaOH.

\begin{align}
\text{NaO}_2 + O &\rightarrow \text{NaO} + \text{O}_2 \\
\text{NaO} + O_3 &\rightarrow \text{Na} + 2\text{O}_2 \\
&\quad + \text{NaO}_2 + \text{O}_2 \\
\text{NaO} + \text{H}_2\text{O} &\rightarrow \text{NaOH} + \text{OH}
\end{align}

Unfortunately, none of these rates had been measured, leading the various modelers to speculate on the importance of each.\textsuperscript{10,12-15} As shown by Sze et al,\textsuperscript{13} the predominant alkali species below 70 km may be NaO, NaO$_2$, and/or NaOH, depending on one's choice for $k_5$, $k_6$, and $k_7$.

In a recent paper by Murad et al,\textsuperscript{8} it was proposed that the reactions of metal hydroxides and superoxides with chlorine compounds between 40 and 70 km may have an impact on the depletion of stratospheric ozone. In the case of sodium, the exothermic bimolecular reactions

\begin{align}
\text{NaOH} + \text{HCl} &\rightarrow \text{NaCl} + \text{H}_2\text{O} \\
\text{NaO}_2 + \text{HCl} &\rightarrow \text{NaCl} + \text{HO}_2
\end{align}
NaO + HCl + NaCl + OH, and possibly  

\[ \text{(10)} \]

NaHCO₃ + HCl + NaCl + H₂CO₃,  

\[ \text{(11)} \]

might be expected to proceed rapidly and act as a sink for Cl, given that NaCl can readily polymerize and condense via heterogeneous nucleation.⁸ Analogous reactions also can occur with Cl and ClO. The inclusion of sodium bicarbonate (in reaction 11) comes about due to the possible occurrence of the reaction

\[ \text{(12)} \]

Murad et al calculated that if the reaction rate of these sodium species with HCl were \(10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\), they might be comparable to the major Cl regeneration mechanism,

\[ \text{(13)} \]

While previously published studies have viewed NaCl as a potential sink for stratospheric chlorine,⁷⁻⁸ more recent analyses by F.S. Rowland²⁵ indicate that photolysis of NaCl may in fact release free Cl. Given the potentially large J values (atmospheric photolysis rate) for this process,²⁵⁻²⁶ reactions (8)-(11) could effectively supplement, rather than remove, reaction (13) as a release mechanism for Cl from the inactive HCl stratospheric reservoir and thereby determine the extent to which ozone might be depleted by chlorine compounds in the stratosphere. However, to fully understand the role of alkali species in the stratosphere one must also consider the effects of NaO₂ and NaOH photodissociation on those processes,¹³,²⁷ as well as homonuclear and heteronuclear sinks for meteoric metal species.

The objective of this program was to provide direct experimental measurements of key rate constants. Obtaining accurate reaction rates for the sodium atmospheric system will enable more accurate modeling of the sodium
emission and density profiles. Once this is completed, these results can be extended toward the larger goal of understanding the chemistry of the more abundant meteor metals.

Over the three years of work on this program, we have measured rate constants for over a dozen alkali reactions and believe that these results will lead to a much improved understanding of the role of meteor metals in atmospheric chemical processes. The remainder of this report details and summarizes our findings. Section 2 is a reprint of our studies of the termolecular recombination of sodium and potassium with molecular oxygen. Section 3 is a preprint of a paper detailing the reaction of Na with O₃ and N₂O, and NaO with O₂. A reprint discussing our measurements of the reaction of NaO and NaOH with HCl comprises Section 4 and a preprint of the analogous reaction of NaO₂ with HCl forms Section 5. Section 6 is a preprint of a paper describing our measurements of the absolute photodissociation cross sections for NaCl. Section 7 describes our work on the measurement of the rate constant for the reaction of NaOH + CO₂ + N. A summary of the results obtained from this program is contained in Section 8 and a listing of papers and presentations made during the course of this contract is given in Section 9.
1.2 References

11. a) Baggaley, W.J., Nature 257, 567 (1975);
    b) Baggaley, W.J., Nature 267, 376 (1977);


SECTION 2

TEMPERATURE DEPENDENT TERMOLECULAR REACTION RATE CONSTANTS FOR POTASSIUM AND SODIUM SUPEROXIDE FORMATION
TEMPERATURE DEPENDENT TERMOLECULAR REACTION RATE CONSTANTS FOR POTASSIUM AND SODIUM SUPEROXIDE FORMATION

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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 using a fast flow reactor. 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 rate constants are found to have the expected negative temperature dependence. The values for \( k (Na + O_2 + M) \) are \( (1.9 \pm 0.4) \times 10^{-10} \) (T/300) \(^{-1} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), with \( M = N_2 \), \( (1.4 \pm 0.3) \times 10^{-10} \) (T/300) \(^{-1} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), with \( M = He \), and \( (1.2 \pm 0.3) \times 10^{-10} \) at T = 324 K with \( M = Ar \), all in units of cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). The values for the corresponding reactions with potassium are larger than those for sodium with \( k (K + O_2 + M) \) = \( (5.4 \pm 0.2) \times 10^{-10} \) (T/300) \(^{-1} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), with \( M = N_2 \), \( (2.0 \pm 0.5) \times 10^{-10} \) (T/300) \(^{-1} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), with \( M = He \), and \( (3.5 \pm 1.0) \times 10^{-10} \) at T = 300 K with \( M = Ar \). The results are compared with other recent measurements from flame and flash photolysis studies and with theoretical expectations based on an energy transfer RRKM mechanism for the NaO_2 activated complex.

Introduction

The chemistry of alkali metals in flames commands our attention for both scholarly and practical reasons. From a scientific standpoint reactions of alkali atoms, with their single valence electron, form a natural test bed to extend our theoretical understanding honed on reactions of atomic hydrogen. Furthermore, the low ionization potentials of alkali atoms open the possibility of electron transfer interaction mechanisms and allow determination of the role of ionic potential surfaces in reaction dynamics. Finally, incredibly sensitive methods of detecting alkali atoms, including hot wire surface ionization, laser induced resonance fluorescence, and laser induced resonance ionization now allow the design of elegant experimental studies for environments ranging from molecular beams to high pressure flames.

From a practical standpoint, gas phase alkali chemistry has long been recognized to be important in flame suppression, and is also involved in the conversion of alkali-containing minerals in coal to alkali sulfates. These sulfates are a major cause of fouling and corrosion of boiler-tube surfaces, heat exchangers, and turbine blades. Alkali atoms introduced into the atmosphere by meteor ablation also play a role in mesospheric chemistry, and it has been suggested that alkali molecules may affect stratospheric ozone reduction through the catalytic chlorine cycle.

However, for all the intrinsic theoretical and experimental interest in alkali reactions, our understanding of the gas phase oxidation chemistry of alkali atoms has only recently progressed, first back to, and then beyond the level gained in the 1930's in pioneering sodam diffusion flame studies by Haber and Sachs, and Bawn and Evans. While these low pressure studies of the reaction of Na with \( O_2 \) showed it proceeded with a termolecular rate constant in excess of \( 10^{-11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), subsequent work (primarily in the mid 1960's) using flame photometric methods by Kaskan and Phillips indicated much lower MO_2 formation rates (M = Na, K) as well as relatively high dissociation energies for the M—O_2 bond (M = Na, Li). Analyses of thermochemical cycles by Herrn and Hirschbach and Alexander clearly indicated that the strengths of M—O_2 bonds deduced from flame photometric data by McEwan and Phillips were greatly overestimated. This was recently confirmed by Figger and co-workers who analyzed observations of chemiluminescence between crossed molecular beams of alkali dimers and molecular oxygen to yield alkali superoxide bond energies.
Reinterpretation of the earlier flame experiments as well as newly performed flame studies are also consistent with lower alkali superoxide bond energies.

The low sodium and potassium termolecular reaction rates deduced from the flame photometry studies are also incorrect. Recently published flash photolysis studies over limited temperature ranges for Li 393 and 463 K, Cs 322 K, Na 724 and 544 K and K 753 and 533 K, as well as flame photometry studies for Na all clearly show fast termolecular rates for alkali superoxide formation.

In this paper we report termolecular rate constants for superoxide formation from sodium and potassium over a much wider temperature range than previously available, yielding the first clear, direct measurement of the temperature dependence of these processes. Third body dependencies are illustrated by separate measurements for N, He and Ar. These measurements were made in a high temperature, fast flow reactor utilizing laser induced resonance fluorescence detection of atomic alkali species. A discussion of these results in terms of their importance in testing termolecular association reaction theory is also presented.

Experimental

The high temperature fast flow reactor used in these experiments has been described in detail previously and is shown in Fig. 1 in the configuration used in this study. Briefly, a 7.26 cm diameter, 120 cm long alumina tube is heated with Kanthal resistance heaters. The helium, argon or nitrogen carrier gas enters the flow tube through two mullite multichannel arrays which both preheat and laminarize the flow upstream of the reaction zone. A sufficient distance (20 cm) is allowed downstream of these arrays for the carrier gas to develop a parabolic flow profile before reaching the reaction zone. Carrier gas flow rates are measured with calibrated rotameters. Total pressures are measured with a capacitance manometer at the downstream end of the reaction zone. Gas temperatures are obtained with a chromel-alumel thermocouple which is movable throughout the reaction zone. The lowest reaction temperatures are slightly above room temperature due to the heating of the carrier gas as it passes over the resistively heated alkali oven. The maximum axial temperature gradient due to this effect over the region in which decay measurements are taken is 10 to 20 degrees depending on flow velocity, pressure and identity of carrier gas. The temperature at the mid point of the reaction zone as measured by the movable thermocouple is used in the data analysis. Axial profiles are more uniform, ±2 to 5 degrees, at elevated temperatures (>400 K) where heating is dominated by the flow tube walls and the mullite arrays. Although the apparatus is capable of temperatures up to 1500 K, experimental considerations as described below limited the upper temperature to 700 K for these studies.

Alkali atoms are generated by heating the pure metal in a 25 mm diameter cylindrical silver plated monel oven to a temperature sufficient to obtain a vapor pressure of 10 to 10 torr within the oven. The oven is mounted on the end of a movable 13 mm od alumina tube concentric to the main flow tube. The vapor is entrained in a flow of carrier gas and introduced into the flow tube in one of two configurations. For the kinetic measurements with O, the oven is placed at a fixed position upstream of the multichannel arrays and the alkali vapor is introduced into the main flow through a 10 cm length of 19 mm diameter silver tubing which passes through the center of the arrays. In the second configuration, the oven is placed downstream of the arrays and is movable throughout the reaction zone to determine the loss of alkali atoms on the reactor walls. The oven temperature is controlled with resistive heating elements independent of the flow tube heaters. Initial alkali atom concentrations in the reaction zone are maintained at less than 10 cm by adjusting the oven temperature and the carrier gas flow rate through the oven.

The alkali atoms are detected by laser induced fluorescence at the downstream end of the flow tube. A Molectron DL14 nitrogen pumped dye laser is used to excite the 4s 5s 4p 5p transition at 404.4 nm for potassium or the 3s 3p 3p transition at 589.0 nm for sodium. Fluorescence is collected using a gated phototube and a computer controlled data acquisition system. The signals are averaged over 100 laser pulses after subtracting for nonfluorescent background contributions and normalizing for pulse to pulse fluctuations in laser intensity. Although no direct calibration of the fluorescence signal was attempted, estimates of...
sensitivity from known phototube and integrator response, measured laser power, and atomic transition probabilities indicate a detection limit for Na of $10^{-6}$ cm$^{-3}$ and for K of $10^{-6}$ cm$^{-3}$ using these transitions.

Molecular oxygen is added through a movable loop injector at distances from 10 to 60 cm upstream of the detection region. O$_2$ flow rates are measured with a calibrated thermal conductivity mass flow meter. The kinetic measurements are conducted under pseudo-first order conditions with $2 \times 10^{14} < [O_2] < 7 \times 10^{15}$ cm$^{-3}$, in large excess compared to the alkali metal atom concentration, yet always <5% of the total gas concentration. First order rate constants are determined for a fixed O$_2$ concentration by recording the change in alkali atom concentration as a function of O$_2$ injector distance.

Corrections for both axial and radial diffusion and wall removal are made using the procedure outlined by Brown. This method is based on a numerical solution of the continuity equation including diffusion, first order chemical reaction and wall removal in a cylindrical tube with fully developed laminar flow. A multiplicative correction factor, obtained for each set of experimental conditions, is used to relate the observed decay to the true first order rate constant. This correction factor is dependent on the wall removal rate constant, $k_w$, and the binary diffusion coefficient for the alkali atom in the carrier gas. Values for $k_w$ are determined in separate experiments at each pressure and temperature by observing the change in atom concentration at the detection point while varying the source oven position. The loss of atoms to the wall was found to be diffusion limited for all the conditions used in this study, implying a surface accommodation coefficient $\gamma > 0.1$. The observed wall loss rate under these conditions may therefore be used to determine the diffusion coefficient $D$ which is then used to determine the correction factor for the reactive flow analysis. The correction factors obtained by this method were in the range $k_{wall}/k_{obs}$ from 1.32 to 1.66, with most lying between 1.60 and 1.63. Under the flow conditions of these experiments, the ratio of reaction to diffusion times is not unlike those encountered in ion-molecule reactions, which also exhibit correction factors on the order of 1.6.

Results and Discussion

Reaction rate constants of atomic sodium with O$_2$ were measured over the temperature range of 320-696 K for nitrogen as the third body collision partner, and over the range of 309-473 K in helium: for potassium, the corresponding temperature ranges were 306-720 K and 286-520 K, respectively. Room temperature measurements were also made in argon for both Na and K. Pressures at each temperature range from 1 to between 5 and 9 torr. Above 700 K, no reliable decays could be measured, because alkali atoms which had accumulated on the walls at lower temperatures began to diffuse into the flow, interfering with the rate measurements.

Using the data for Na + O$_2$ + (He) as an example, we see in Fig. 2 that the first-order (logarithmic) decays of signal with reaction time are linear for over a factor of 100. Plots of a series of first-order rate constants (corrected for wall and diffusional effects) versus [O$_2$] are illustrated in Fig. 3. Second-order rate constants derived from these are then plotted vs. total number density and the third-order rate constants are determined from the slopes of these plots. In most cases, these lines intersect the origin to within the statistical uncertainties of the fit $1\pm 10$ s$^{-1}$. For Na + O$_2$ + (N$_2$), a small positive intercept is observed at all temperatures. The cause for the intercept is unclear. An explanation sometimes given for such behavior is that the wall acts as a stabilizing third body and adds a pressure independent component to $k_{11}$. However, this explanation would appear unlikely in these experiments given the near unit efficiency for wall removal of all alkali species. An alternative explanation is that insufficient diffusional mixing of the injected O$_2$ could lead to underestimation of $k_{11}$ at higher pressures, resulting in an apparent intercept.

![Fig. 2: Pseudo-first order decay of Na fluorescence signal vs. reaction distance for M = He at 309 K and 5.05 torr. $[O_2] = 1.09$ (a), 3.36 (b), 7.29 (c), 14.3 (d), 26.6 (e), units of $10^{14}$ cm$^{-3}$. The estimated relative standard deviations for these points range from 1% to 4%.](image-url)
in the $k^{11}$ vs. pressure plots. However, calculations of mixing length indicate that this effect should not be significant even at the highest pressure (450 torr) in these studies.

The three-body association rate constants as a function of temperature for various third body collision partners are shown for sodium in Fig. 4 and for potassium in Fig. 5. The data can be described by an expression of the form $k^{11}(T) = AT^{-n}$. The results of nonlinear least-square fits to this function are found in Table 1. For sodium in helium and nitrogen, and for potassium in helium, a simple $T^{-1}$ representation could also be used. However, the results for potassium in nitrogen show a somewhat weaker temperature dependence, best represented by $T^{-0.363 \pm 0.05}$, although this difference is not significant within the statistical uncertainties of the data.

The expressed total experimental uncertainties, including allowance for systematic errors, can be estimated as the square root of the sum of the squared individual uncertainties due to: a) flow velocity, temperature, pressure, and concentration calibration factors, 5%; b) the precision in determining the coefficient $A$ in the expression for $k^{11}(T)$, 17%; and c) the uncertainty in the correction of observed first-order decays for wall removal and diffusional effects, 10%.

Table 1 also contains other determinations of $k$. Husain and Plane[25] used a flash photolysis system to generate alkali atoms from KI and NaI and followed the decay of K and Na by atomic resonance absorption. They observed no temperature dependence over their limited temperature range (724 K and 844 K) for the Na + O$_2$ + M reaction.

Fig. 4. Plot of ln $k(T)$ vs. In T for the reaction Na + O$_2$ + M, with M = N$_2$ (circles), He (triangles), and Ar (square) for this work. The solid lines are least-square fits to these data. The + and $\times$ symbols represent data for M = N$_2$ and He, respectively from reference 25. The dashed line M = flame gases is from reference 25.

Fig. 5. Plot of ln $k(T)$ vs. In T for the reaction K + O$_2$ + M, with M = N$_2$ (circles), He (triangles), and Ar (square). The solid lines are least-square fits to these data. The + and $\times$ symbols represent data for M = N$_2$ and He, respectively from reference 25.
A substantially larger variation with temperature was obtained for their K + O₂ + M study although they arbitrarily fit their data to a T⁻¹ dependence. The agreement between their values and the slightly extrapolated temperature dependent rate constants for both reactions from this work is satisfactory, especially considering the very different methods employed. This comparison is shown in Figs. 4 and 5.

Hynes et al. have studied the Na + O₂ + M reaction in experiments using laser induced fluorescence to measure Na and OH profiles under fuel lean conditions in H₂/O₂/N₂ flames. A detailed kinetic model assuming reasonable values for rate constants for the reactions interconnecting the species Na, NaO*, NaOH is used to determine the best fit to the observations. Their optimum value of k( Na + O₂ + M), assuming a T⁻¹ temperature dependence, is shown in Fig. 4, and is lower by about a factor of 4 compared to the extrapolated fit from this work. The much earlier diffusion flame studies corrected identified the Na + O₂ + M reaction to be fast for a three body process. The later and more extensive study by Hawn and Evans obtained a value at 533 K which is higher by a factor of 3 than this study. They also observed a fall-off behavior for their second order rate constant with pressure above about 10 torr and present their results in terms of an energy transfer mechanism using a Lindemann-type expression to interpret their data. This fall-off behavior was not observed by Hynes and Plane who show linear plots of k versus pressure from 25 to 150 torr. Their effective bimolecular rate at 150 torr and 724 K for the Na + O₂ + (N₂) reaction of 2.2 x 10⁻¹² cm³ s⁻¹ is nearly equal to the high pressure limit inferred by Hawn and Evans of 3 x 10⁻¹⁵ cm³ s⁻¹. It thus appears that the pressure dependence observed by Hawn and Evans

---

**TABLE I**

Comparison of measured rate constants for Na + O₂ + M → NaO + M

and K + O₂ + M → KO₂ + M

<table>
<thead>
<tr>
<th>Reference</th>
<th>Alkali</th>
<th>Method</th>
<th>M</th>
<th>P (torr)</th>
<th>T(K)</th>
<th>k (cm³ O⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>Na</td>
<td>Fast Flow Reactor</td>
<td>N₂</td>
<td>0.8-8.0</td>
<td>320-700</td>
<td>$(1.9 ± 0.4) \times 10^{-9}$ (T/300)⁻¹¹⁺³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Laser Induced</td>
<td>He</td>
<td>1.0-8.1</td>
<td>310-470</td>
<td>$(1.4 ± 0.3) \times 10^{-9}$ (T/300)⁻⁹⁺²⁻³</td>
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<tr>
<td></td>
<td></td>
<td>Fluorescence</td>
<td>Ar</td>
<td>1.0-3.0</td>
<td>324</td>
<td>$(1.2 ± 0.3) \times 10^{-9}$</td>
</tr>
<tr>
<td>Husain and</td>
<td>Na</td>
<td>Flash Photolysis</td>
<td>N₂</td>
<td>25-150</td>
<td>724</td>
<td>$1.1 \times 10^{-7}$</td>
</tr>
<tr>
<td>Plane²⁵</td>
<td></td>
<td>Resonance</td>
<td></td>
<td></td>
<td>844</td>
<td>$1.0 \times 10^{-7}$</td>
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<tr>
<td></td>
<td></td>
<td>Absorption</td>
<td>He</td>
<td>30-120</td>
<td>724</td>
<td>$0.53 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>He</td>
<td></td>
<td></td>
<td>844</td>
<td>$0.67 \times 10^{-7}$</td>
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<tr>
<td>Hynes et al.</td>
<td>Na</td>
<td>Flame Studies with Laser Induced Fluorescence</td>
<td>H₂O/O₂/N₂</td>
<td>760</td>
<td>1650-2400</td>
<td>$2 \times 10^{-7}$ T⁻¹</td>
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<tr>
<td>Bawn and</td>
<td>Na</td>
<td>Diffusion Flame</td>
<td>N₂</td>
<td>4-25</td>
<td>533</td>
<td>$4.6 \times 10^{-8}$</td>
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<tr>
<td>Evans¹⁵</td>
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<td></td>
</tr>
<tr>
<td>This work</td>
<td>K</td>
<td>Fast Flow Reactor</td>
<td>N₂</td>
<td>1.0-6.0</td>
<td>302-720</td>
<td>$(5.4 ± 0.2) \times 10^{-9}$ (T/300)⁻⁹⁺²⁻³⁰</td>
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<tr>
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<td></td>
<td>Laser Induced</td>
<td>He</td>
<td>1.0-6.0</td>
<td>296-520</td>
<td>$(2.0 ± 0.5) \times 10^{-9}$ (T/300)⁻⁹⁺²⁻³⁰</td>
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<tr>
<td></td>
<td></td>
<td>Fluorescence</td>
<td>Ar</td>
<td>1</td>
<td>300</td>
<td>$(3.5 ± 1.0) \times 10^{-9}$</td>
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<tr>
<td>Husain and</td>
<td>K</td>
<td>Flash Photolysis</td>
<td>N₂</td>
<td>40-160</td>
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<td>$2.9 \times 10^{-6}$</td>
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<td>Resonance</td>
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<td></td>
<td>873</td>
<td>$1.4 \times 10^{-6}$</td>
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<tr>
<td></td>
<td></td>
<td>Absorption</td>
<td>He</td>
<td>40-160</td>
<td>753</td>
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<tr>
<td></td>
<td></td>
<td>He</td>
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<td>$0.96 \times 10^{-6}$</td>
</tr>
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</table>
may have been an artifact of their experimental diffusion flame technique. No curvature was observed in our lower pressure $P \geq 8$ torr conditions of this study and under these conditions, the recombination reaction appears to be in its low pressure, third order, limit.

In this limit, the recombination rate constant can best be calculated using unimolecular theory, in which second-order rate constants for unimolecular decomposition are related through the equilibrium constant to the third order (low pressure) association rate constants. The unimolecular rate constants are obtained using simplified equations of Troe based on RRKM theory. The recombination rate constant can be expressed as the product of a strong collision rate constant $k_{rcc,m}$ and a weak collision deactivation efficiency term $\beta_c$.

$$k_{rec} = k_{rcc,m} \beta_c$$

In effect, $\beta_c$ is a term expressing the efficiency by which (NaO$_2$)* is stabilized upon collision. In the absence of detailed state-to-state energy transfer rates, $\beta_c$ is an adjustable parameter which depends on the average change in internal energy of the transition state complex per collision, $\langle \Delta E \rangle$, so that

$$\beta_c = \frac{\langle \Delta E \rangle}{1 - \beta_c^{1/2}} F_{E}RT$$

$F_{E}$ is a correction term for the energy dependence of the density of states in the transition complex. Using a value of 163 kJ mol$^{-1}$ for the Na—O$_2$ bond energy, Patrick and Golden have calculated $k_{rcc}$ for Na + O$_2$ + (He)$_3$ at 300 and 700 K. The computations result in $k_{rcc,m}(300 \text{ K}) = 7.5 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$ for $M = \text{He}$. Thus, a value of $\beta_c = 0.18$ is required to reproduce the experimental results at 700 K. $k_{rcc,m}(700 \text{ K}) = 4.2 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$, suggesting a value of $\beta_c = 0.09$ if $\langle \Delta E \rangle$ is assumed to be independent of temperature. Extrapolation of the experimental value for helium to 700 K results in an observed $\beta_c = 0.14$, in good agreement, considering the simplified assumptions of this approach.

This unimolecular approach has been shown to be fairly reliable in calculating termolecular association rate constants for a variety of species. The values of $\beta_c$ for $M = \text{N}_2$ and Ar tend to lie in the range of 0.1–0.5. The calculations for Na + O$_2$ in helium agree quite well with these numbers, given that one might expect helium to be somewhat less efficient than N$_2$ in quenching the excited intermediate. For the similar reaction H + O$_2$ + (N$_2$), the calculations also perform well, giving $\beta_c = 0.06$, even though the rate constant for this reaction, $3.9 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ at 300 K, is approximately 30 times slower than the corresponding sodium reaction.

In extrapolating our measured rate constants to higher pressures, it is important to understand the fall-off behavior as the reaction mechanism goes from its low pressure third order limit to its high pressure second order limit. A method for calculating the fall-off parameter based on RRKM theory has been developed by Luther and Troe. Using their approach, the bimolecular rate constant in the transition region may be calculated as

$$k^H = \frac{k_s k_{[M]} F_{E} \cdot \text{ln}(k_s k_{[M]} k_{rec})^{1/2}}{k_s + k_{[M]}^{1/2}}$$

where $k_s$ and $k_{[M]}$ are the high pressure and low pressure limiting rate constants, respectively. The broadening parameter, $F$, is dependent on the molecular structure of the adduct and typically is on the order of 0.6 for small molecules. The Patrick and Golden calculation for NaO$_2$* gives $F = 0.3$.

In order to assess the fall-off behavior, the association rate $k_s$ may be estimated from the dynamics of the Na + O$_2$ encounter. Alkali atom reactions are often described in terms of their ionic character which leads to very fast reaction rates via an electron jump mechanism. Ionic forces in the alkali-oxygen associations, however, are not as dominant as in other alkali atom reaction mechanisms. Although the approaches differ, they do both have an electron jump transfer from the incident covalent potential surface to an ionic surface, electron jump mechanism, the crossing distance ($r_c$) is relatively small as compared with alkali-halogen systems and the overall association rate is dominated by the dispersion interaction on the covalent potential surface. This is illustrated by comparing the rate constant based on the product of the mean collision velocity and the electron jump cross section modified to account for the dispersion and angular momentum terms in the covalent potential function to a rate constant computed from a close collision model in which all collisions surmounting the angular momentum barrier of a Cr$^*$ potential contribute to the rate. For Na + O$_2$ at 300 K, an electron jump rate constant $r_e = 2.6 \text{ A}$ is $1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, while the close collision constant is $5.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Thus, it appears that the rate of intermediate complex formation for reaction (2) is governed by long range dispersion forces as found in most covalent systems. Once formed, however, these intermediates are certainly alkali-O$_2$ ion pairs. In either case, the association rate constant is expected to be fast with a value for $k_s > 10^{10} \text{ cm}^3 \text{ s}^{-1}$.

Using a value for $k_s = 2 \times 10^{10} \text{ cm}^3 \text{ s}^{-1}$, Eq (3) may be used to estimate the ratio of the observed rate constant, $k_{rec}$, to the true third order low pressure limit, $k_s$. At the maximum density
our studies, \(1.6 \times 10^{-7} \text{ cm}^{-3}\), one obtains \(k_{ab}/k_{c} = 0.93\) which indicates that our experiments are essentially in the low pressure limit. For the conditions of Husain and Plane\(^{25}\) (150 torr, 724 K), this same calculation would predict \(k_{ab}/k_{c} = 0.87\). For the combustion conditions with \(P = 760\) torr, \(T = 2000\) K applicable to the Hynes et al. study,\(^{25}\) one obtains \(k_{ab}/k_{c} = 0.89\). Thus, the large value for \(k_{c}\) would indicate that both of these studies are also essentially in the low pressure limit with regard to the recombination reaction.

Acknowledgments

The authors would like to thank Dr. F. Kaufman for many helpful discussions, and Drs. D. Golden and R. Patrick for performing association rate calculations for sodium. The technical assistance of W. Goodwin is greatly appreciated. This work was supported by the Air Force Geophysics Laboratory under Contract Number F19628-83-C-0010. by the Chemical Manufacturers Association under Contract Number FC82-10. and by the Chemical Manufacturers Association under Contract Number FC82-401.

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COMMENTS

A. Fontijn, Rensselaer Polytechnic Institute, USA.

You mentioned some work you did on the temperature dependence of reactions of NaOH and NaCl (e.g., with H). How were the reactants generated in these experiments?

Authors’ Reply. We have recently completed a study of rate constant measurement for the reactions of NaOH + HCl → NaCl + H₂O and Na( + HCl → NaCl + OH. Both alkali reactants are formed from the gas phase reaction of atomic sodium and hydrogen peroxide. Measurement of the alkali products was done by converting the alkali molecule to atomic sodium in the detection zone (by addition of excess atomic hydrogen) and detection using laser induced fluorescence.

REFERENCE

SECTION 3

DETERMINATION OF THE ABSOLUTE RATE CONSTANTS FOR
THE ROOM TEMPERATURE REACTIONS OF ATOMIC
SODIUM WITH OZONE AND NITROUS OXIDE

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October 1985

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DETERMINATION OF THE ABSOLUTE RATE CONSTANTS FOR THE ROOM TEMPERATURE REACTIONS OF ATOMIC SODIUM WITH OZONE AND NITROUS OXIDE

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ABSTRACT

The reaction of atomic sodium with ozone is important in describing the chemistry of the lower thermosphere and upper mesosphere, and is directly related to the observed sodium D-line emissions at 589 nm in these regions of the atmosphere. We report a room temperature rate constant of this reaction to be $(3.1 \pm 0.4) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The rate constant for the NaO + O$_3$ reaction is determined to be about $2 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, with 0.7 $\pm 0.2$ of the products being NaO$_2$ + O$_2$, and the remainder Ne + 2O$_2$. We have also measured the rate constant for Ne + N$_2$O + NaO + N$_2$ to be $(7.7 \pm 0.9) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 295 K. The impact of the reactions with ozone on the mesospheric chemistry of alkali metals of meteoric origin is discussed.

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INTRODUCTION

The reaction of atomic sodium with ozone is of fundamental importance in understanding the chemistry of ablated meteor metals in the lower thermosphere and upper mesosphere. It is the major sink for atomic sodium above 85 km and knowledge of its rate constant is critical for modeling the 70-95 km layer and in understanding the processes leading to the sodium D-line Chapman emissions.\(^1\)-\(^{15}\) Despite these significant modeling efforts, prior to 1982 almost no kinetic data existed for most of the reactions used in these models. The earlier models utilized rate constants which were estimated from analogy with atomic hydrogen reactions. In 1976, Kolb and Elgin\(^{16}\) pointed out that the alkali metal atom reaction rates are often much faster than the analogous hydrogen reactions, due to long-range "electron-jump" processes.\(^{17}\) However, it has only been in the last few years that direct measurements of alkali rate constants have been made to confirm these suggestions.\(^{18\text{-}25}\)

In this paper we report room temperature measurements of the rate constants for the reactions of atomic sodium with ozone and nitrous oxide,

\[
Na + O_3 + NeO + O_2 \rightarrow NaO + O_2 + Ne \quad \Delta H_f = -167 \pm 42 \text{ kJ mole}^{-1} \quad (1)
\]

\[
Na + N_2O + NeO + N_2 \rightarrow NaO + NeO + N_2 \quad \Delta H_f = -106 \pm 42 \text{ kJ mole}^{-1} \quad (2)
\]

We also present information on the approximate rate constant and product branching ratio for the reaction of sodium monoxide with ozone,
These and other recent results will help to provide a clearer picture of the chemistry of meteor metals in the mesosphere.

**EXPERIMENTAL**

Rate constant determinations are made in a fast-flow reactor, which is illustrated in Figure 1 and has been described in detail elsewhere. Briefly, the flow reactor is a 7.26-cm-diameter, 120-cm-long alumina tube, with four perpendicular side arms at the tube exit which permit optical detection of the flow species. Helium carrier gas is added at the entrance of the flow tube through mullite multichannel arrays which laminarize the flow. Gas volumetric flow rates are determined with calibrated thermal conductivity type mass flow meters. A calibrated MKS Baratron Model 310-BHS capacitance manometer (0.8% accuracy) is used to measure pressure.

Alkali atoms are generated by heating a 1 g sample of metallic sodium in a 2.5-cm-diameter cylindrical monei oven to a temperature commensurate with attaining a vapor pressure of $10^{-6}$ to $10^{-4}$ torr within the oven. The oven is enclosed in a 4-cm-diameter water-cooled sheath to prevent heating of the main flow carrier gas. The sodium vapor is entrained in a small flow of helium and introduced into the flow tube, where dilution by the carrier gas in the main flow tube restricts the sodium concentration in the reaction zone to no more than $10^{10}$ cm$^{-3}$.
Ozone is generated just before each experiment in a commercial ozonator (Welsbach Model T-408) and collected on silica gel at 196 K. It is then pumped on for a few hours to remove any remaining O₂. It is eluted into the flow tube quartz injector with a controlled flow of helium. The ozone flow rate is determined by UV absorption at 253.7 nm (using a Hg pen lamp and interference filter) in a 1.00-cm-long stainless steel cell. The partial pressure is measured using Beer's law and the absorption cross section of 1.15 x 10⁻¹⁷ cm². This calculation uses a cell temperature about 7°C above room temperature, due to heating of the cell by the lamp. The total pressure in the cell, typically 700 - 760 torr, is measured with a Validyne pressure transducer. There are negligible losses of ozone during transport, via Teflon tubing, to the flow tube, in the 2-meter-long quartz injector, or along a 72 cm length of the flow tube. This was ascertained by a series of calibrations in which a second absorption system was set up to measure O₃ partial pressures in the flow reactor detection zone. This system consisted of a mercury resonance lamp (Spectroline), with the 253.7 nm line isolated by a 0.074 m monochrometer (PTR Optics), and measured by a photodiode using phase-sensitive detection. After correction for differing path lengths, flows, etc., the O₃ concentration in the flow tube matched that in the cell to within 10%, over all flow conditions used during the actual rate experiments.

Detection of atomic sodium was accomplished in two ways, either by resonance lamp fluorescence with phase sensitive detection, or by laser-induced fluorescence using a gated integrator. At the low levels of atomic sodium reaching the detection region optical trapping is not a problem. In both cases, the data were fed to an IBM X/T computer for on-line collection and analysis.
All rate measurements are performed with $O_3$ or $N_2O > Na$, ensuring pseudo-first order kinetic conditions. Reaction times were varied from approximately 3 - 40 ms for the ozone reaction and 1 - 30 ms for the nitrous oxide reaction. Data analysis and corrections for wall loss and diffusion effects were made as described in previous alkali reaction studies.\textsuperscript{19,28}

The purities of chemicals used in these experiments are as follows: sodium metal, 99.95\% (Alfa); helium for $O_3$ and Na flows, 99.998\%; helium for main flow, 99.995\%; oxygen, 99.99\%; hydrogen chloride, 99.99\%; nitrous oxide, 99.0\%; and carbon monoxide, 99.8\%.

**RESULTS**

Na + $O_3$

The reaction of atomic sodium with ozone forms sodium monoxide as a product,

\[ Na + O_3 \rightarrow NaO + O_2 \]  \hfill (1)

However, the NaO subsequently reacts with ozone, to produce either NaO$_2$ or to reform atomic sodium,

\[ NaO + O_3 \rightarrow NaO_2 + O_2 \quad \Delta H_f^\circ = -282 \pm 47 \text{ kJ mole}^{-1} \]  \hfill (3a)

\[ + Na + 2O_2 \quad \Delta H_f^\circ = -119 \pm 42 \text{ kJ mole}^{-1} \]  \hfill (3b)
If the branching to 3b is significant, the observed decays of sodium would not be linear (on a semilog plot of signal versus reaction time), and a more complicated data analysis would be required.

We suppressed this possible complication by adding hydrogen chloride along with the main carrier flow in concentrations exceeding that of O₃ by a factor of 100. The reaction of NaO with HCl produces nonreactive NaCl,

\[ \text{NaO} + \text{HCl} \rightarrow \text{NaCl} + \text{OH}, \]  

so that the observed semilog decays of atomic sodium become linear and result only from reaction 1.

Decays of Na for seven concentrations of ozone covering the range of 4.04-36.3 \( \times 10^{12} \) cm\(^{-3}\) are shown in Figure 2. These were made for pressures of 1.95-2.31 torr and flow velocities of 1380-1635 cm s\(^{-1}\) at 293 K. These plots are linear for over four orders of magnitude of sodium concentration. The first order decay rates obtained from the slopes of the lines, corrected for diffusion and wall loss (with factors ranging from 1.66 to 1.90), are plotted versus the corresponding O₃ concentration in Figure 3. A least-squares fit to the slope of this line, weighted by the uncertainties in each point, results in a rate constant value of \((3.1 \pm 0.4) \times 10^{-10} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for reaction 1. The uncertainty expressed includes precision errors (one standard deviation), as well as estimated errors in accuracy.

Our Na + O₃ results are in good agreement with recent measurements by Husein et al.\(^{21}\) who measured this rate constant to be \((4 \pm 4, -2) \times 10^{-10} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 500 K using atomic resonance spectroscopy following pulsed
Irradiation. However, they did not take into account any effects of the NaO + O₃ reaction, so that their result can be considered only qualitatively correct. Our results are a factor of two smaller than that measured by Ager and Howard,¹⁵ using very similar experimental techniques. The reason for this discrepancy is unclear.

A series of measurements were also made without adding HCl. We attempted to fit the observed curvature in these decays with a model containing reactions 1, 3a, and 3b. The analytic solution for [Na] is a sum of two exponential decays,²⁹

\[ [\text{Na}(x)] = ae^{-bx} + ce^{-dx}, \]

where

\[ a, b, c, \text{ and } d \] are algebraic combinations of \( k_1, k_{3a}, \) and \( k_{3b}, \) and \( x = [O_3]t. \) Sodium profiles (as measured at the detector) from this calculation are plotted as a function of \([O_3]t\) in Figure 4, along with the experimental data taken without HCl. The values used for the rate constants are those uncorrected for diffusion effects, as we are trying to fit raw data. However, these corrections are straightforward, since they are approximately independent (1.66-1.90 for this data) of the magnitude of the observed reaction rate in the situation of unit wall loss and fast radial diffusion.²⁸ We also assume that the wall loss rate and diffusion corrections are the same for all of the molecular sodium species in the calculation. One set of solutions is shown in Figure 4, using the measured value of \( k_1 \) and a value of \( k_3 \) equivalent to \( 2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \) The curves illustrate how the decay varies as a
function of $k_{3a}/k_3$. Although the fit for $k_{3a}/k_3 = 0.7$ is good, the shapes of the curves vary with $k_3$. As $k_3$ is decreased, the curves break away from the $k_{3b} = 0$ curve (e) at larger values of $[O_3]t$, and flatten out more rapidly for corresponding values of $k_{3a}/k_3$. Given the approximations in this calculation, the scatter in our data, and the ambiguity in fitting these curves, we conclude that $k_3$ is approximately $2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ and that $k_{3a}/k_3 = 0.7 \pm 0.2$.

**NaO + N_2O**

The reaction of atomic sodium with nitrous oxide is much slower than with ozone. Furthermore, nonlinearities in the semilog plots of signal versus reaction time are not observed, demonstrating that the reaction of NaO with N_2O does not have a significant atomic sodium product channel. Thirteen sodium decays were measured (of which, for clarity, seven are shown in Figure 5) for a nitrous oxide concentration range of $3.97 - 95.4 \times 10^{13} \text{ cm}^{-3}$. The flow velocity for these experiments was either 840 or 1240 cm s$^{-1}$, at corresponding pressures of 1.52 and 2.23 torr. The overall results were the same for both operating conditions. The corrected first order decays obtained from these lines (with correction factors ranging from 1.62 to 1.82) are plotted versus $[N_2O]$ in Figure 6. The resultant rate constant for this reaction is $k_2 = (7.7 + 0.9) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ at 295 K. This is in excellent agreement with an extrapolation to room temperature of results of Husein and Marshall.$^{24}$ Their value of $k_2 = (1.9 \pm 0.3) \times 10^{-10} \exp (-12.5 \pm 0.6 \text{ kJ/mole/RT}) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$, was measured over the temperature range.
DISCUSSION

The results of this work confirm that the Na + O₃ reaction rate constant approaches the gas kinetic limit, agreeing remarkably well with 3.3 \times 10^{-10} cm³ molecule⁻¹ s⁻¹ predicted by Kolb and Elgin¹⁶ using an electron-jump model. Unlike ozone, N₂O is an 18-electron closed shell molecule and despite a large exothermicity, exhibits a moderate activation energy,²⁴ leading to a lower value for the room temperature rate constant. This activation energy might be explained by the increase of reactive cross section with increasing vibrational excitation, in correlation with the increasing stability of a bent N₂O⁻ structure as predicted by Walsh's rules, as previously observed with reactions of N₂O with Ba and Sm.³⁰-³²

The fate of neutral sodium as it enters the mesosphere is illustrated in Figure 7. Above 85 km, it reacts primarily with ozone to form NaO, which subsequently reacts with atomic oxygen to produce both ground state and electronically excited sodium atoms. This latter process leads to the observed D-line emission of sodium at 589 nm.¹ Below 85 km, the termolecular recombination with O₂ dominates, forming NaO₂. This molecule can react with atomic oxygen to form NaO, which is rapidly converted to NaOH by reaction with H₂O.²⁵ It is still uncertain whether NaOH is the major alkali species below 70 km, or if both NaO₂ and NaOH are significant. This depends on the rate constant for NaO₂ + O → NaO + O₂, and on the photolysis rates for NaO, NaO₂ and NaOH, which have not yet been directly measured.
In conclusion, we have confirmed that the reaction of ozone with atomic sodium at room temperature is near its gas kinetic limit, strengthening the recent model predictions for the partitioning of alkali species in the mesosphere and upper stratosphere. Although much remains to be done, our understanding of atmospheric chemical cycles involving metals of meteoric origin has significantly improved in the past few years.
ACKNOWLEDGEMENTS

We gratefully acknowledge the many contributions of Dr. Mark Zahnisier, Warren Goodwin, and the late Dr. Frederick Kaufman, as well as helpful discussions with Drs. William Swider, Edmond Murad, and Charles Gallagher of the Air Force Geophysics Laboratory.

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REFERENCES


FIGURE CAPTIONS

1. Illustration of fast flow reactor in which these rate constant measurements were made.

2. Pseudo first-order decays for the Na+O₃ reaction in the presence of hydrogen chloride. [O₃] = 5.04, (○), 5.34 (●), 8.64 (□), 17.2 (■), 17.3 (△), 21.8 (∆), 36.3 (◇); units of 10¹¹ cm⁻³.

3. Dependence of corrected pseudo-first-order rate constant on O₃ concentration at 293 K.

4. Plot of computed curves for observed Na decay as a function of [O₃] for a variety of values of k₃a/k₃. This calculation uses k₁ = 3.1 x 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, and k₂ = 2 x 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹.
   k₃a/k₃ = a) 0; b) 0.5; c) 0.7; d) 0.9; e) k₃b = 0.

5. Pseudo-first-order decays for the Na+N₂O reaction. [N₂O] = 3.97 (○), 10.8 (●), 24.0 (□), 35.5 (■), 48.7 (△), 61.2 (∆), 95.4 (◇); units of 10¹³ cm⁻³.

6. Dependence of corrected pseudo-first-order rate constant on N₂O concentrations at 295 K.

7. Schematic Diagram for Mesospheric Sodium Chemistry.
Figure 5

RELATIVE SIGNAL

REACTION TIME (msec)

3-20
Na + N₂O → NaO + N₂

\[ k'(\text{sec}^{-1}) \]

\[ [\text{N}_2\text{O}] \left(10^{14} \text{ molecules cm}^{-3}\right) \]

3-21
SECTION 4

GAS-PHASE REACTION RATE OF SODIUM HYDROXIDE
WITH HYDROCHLORIC ACID
Gas-Phase Reaction Rate of Sodium Hydroxide with Hydrochloric Acid

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The reactions of metallic species introduced into the atmosphere by meteor ablation may play a significant role in stratospheric chemistry. In particular, it has been suggested that the reaction of NaOH with HCl might affect the concentration of odd chlorine, thus having an impact on the ozone balance. This paper describes the first measurement of this reaction rate constant. At 308 K, we find that \( k \approx (2.8 \pm 0.9) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}. \) As a result of the methods developed to perform this measurement, we have also determined estimates of the following room temperature rate constants in units of \( \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}: \)

- \( k(\text{NaO} + \text{HCl} \rightarrow \text{NaCl} + \text{OH}) \approx 2.8 \times 10^{-10}, \)
- \( k(\text{NaOH} + \text{H} \rightarrow \text{Na} + \text{H}_2\text{O}) > 4 \times 10^{-13}, \)
- \( k(\text{NaCl} + \text{H} \rightarrow \text{Na} + \text{HCl}) \approx 5 \times 10^{-11}, \)
- \( k(\text{Na} + \text{H}_2\text{O}) \approx 6.9 \times 10^{-11}, \)

where approximately 0.6 of the reactions produce NaOH + OH, with the remainder forming NaO + H₂O.

Introduction

Metallic elements volatilized during meteor entry into the Earth's upper atmosphere play a significant role in the structure of the D and E regions of the ionosphere, and, at least in the case of sodium, the visible day and nightglow emissions from the mesosphere and lower thermosphere. Recently, it was suggested...

In fact, until 2 years ago, even this reaction was thought to be 
~1000 times slower^{10} than the value found in the more recent 
measurements.

From the recent modeling work\cite{3,8,10,13,21-22} and comparison of 
these models with atmospheric measurements,^{12,14-15} neutral 
sodium is believed to be transformed via a series of chemical re-
actions involving NaO and NaO$_2$ intermediates to NaOH. A 
survey of the relevant literature\cite{3,8,10} provides a fairly complete 
list of possible neutral sodium reactions of importance, and a 
simplified schematic diagram of these reactions is shown in Figure 
1.

Neutral sodium appears in a range between 110- and 70-km altitude. As 
shown in Figure 1, the main removal mechanisms are by reaction with O$_2$ or O$_3$, the latter used by Chapman\cite{23} to 
explain the Na nightglow. We have recently completed tem-
perature-dependent measurements of the reaction rates with O$_2$ 
in our laboratory which show that this reaction proceeds with a 
fast three-body rate constant of 1.9 X 10$^{-30}$ cm$^6$ s$^{-1}$ with N$_2$ as 
the third body at 300 K.\cite{18} This leads us to believe that most of 
the Na in the lower mesosphere is converted to NaO$_2$, since the 
three-body recombination rate with O$_3$ exceeds even a gas kinetic 
two-body rate with O$_3$ below 80 km. Since none of the remaining 
rates have ever been measured, the rest of the mechanism (as 
proposed by various models) is speculative. However, the dominant 
sodium species which leave the mesosphere and enter the stra-
tosphere are probably NaOH and/or NaO$_2$.

The fate of NaOH is very uncertain. Indeed, only in the past 
few years has NaOH been recognized as a major reaction product. 
Ferguson\cite{6} suggested that it forms NaOH cluster ions of the form 
H$^+$[NaOH]$_2$(H$_2$O)$_m$, which either may be rained out from the 
troposphere or removed in the stratospheric aerosol layer. In a 
recent paper by Murad et al.,\cite{24} it was proposed that the reactions 
of metal hydroxides (and superoxides) with chlorine compounds 
between 40 and 70 km may have an impact on the depletion of 
stratospheric ozone. In the case of sodium, the exothermic bi-
molecular reactions

$$
\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}
$$

(2) 

$$
\text{NaOH} + \text{ClO} \rightarrow \text{NaCl} + \text{HO}_2
$$

(3) 

$$
\text{NaOH} + \text{Cl} \rightarrow \text{NaCl} + \text{OH}
$$

(4) 

might be expected to proceed rapidly and act as a sink for Cl, 
given that NaCl can readily polymerize and condense via heter-
ogeneous nucleation. Murad et al. calculated that if k$_2$ were 
~10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, then the reaction of NaOH with HCl 
would be comparable to the major recognized Cl regeneration 
mechanism

$$
\text{OH} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2\text{O}
$$

(5) 

While previously published studies have viewed NaCl as a potential 
sink for stratospheric chlorine,\cite{3,8,10} more recent analyses by Row-
land\cite{24} indicate that photolysis of NaCl may in fact release free 
Cl. Given the potentially large J values (photolysis rates) for this 
process,\cite{24} reactions 2-4 could effectively supplement reaction 5 
as a release mechanism for Cl from the inactive HCl stratospheric 
reservoir and thereby determine the extent to which ozone might 
be depleted by chlorine compounds in the stratosphere. However,
Gas-Phase Reaction of NaOH with HCl

Figure 2. Schematic view of the flow tube

to understand fully the role of alkali species in the atmosphere, just consider the effects of NaO₂ and NaOH photo-Dissociation on these processes.

The purpose of this study is to provide a direct experimental rate measurement of the reaction NaOH + HCl → NaCl + H₂O, which serves as a starting point for understanding the stratospheric role of sodium and other meteor metals. Only by obtaining accurate, directly measured rate constants can we hope to understand atmospheric metallic chemistry, and, in particular, how this chemistry affects the ozone balance.

Experimental Section

Very little gas-phase research has been done on alkali hydroxides because they are difficult to vaporize, are extremely corrosive, and readily dimerize in the gas phase. In addition, there are no established detection techniques sensitive enough to allow kinetic analyses of alkali hydroxide reactions. With this in mind we have taken an indirect approach for producing and detecting NaOH, i.e., chemical production of NaOH by the reaction of atomic sodium with hydrogen peroxide, and detection of NaOH by chemical conversion back to atomic sodium, which is then observed by laser-induced fluorescence.

The measurements were performed in the Aerodyne high-temperature fast-flow reactor, which is fully described in ref 29 and whose relevant features are illustrated in Figure 2. Briefly, a 7.26-cm-diameter, 120-cm-long alumina tube is used, fitted with Kanthal heater elements which can radiatively heat the tube over the temperature range 294–1500 K. Four perpendicular alumina side arms at the tube exit permit detection of flow species by a variety of optical techniques, including laser- or resonance lamp-induced fluorescence, infrared absorption (either broad band or high resolution), and observation of chemiluminescence. Gas temperatures are obtained with chromel-alumel or shielded W-5% Re–W-26% Re thermocouples. Extensive calibrations indicate that the temperature can be measured with an accuracy of ±10 K over the entire operating range of the reactor for flow Reynolds numbers below 5000; for the current experiments they are typically below 50. The gas is pumped by a Kinney KMKB 1602 mechanical pump and Roots blower with an effective pumping speed of 450 L s⁻¹. The helium carrier gas is added at the entrance of the flow tube through multi-channel arrays which laminarize the flow. These are ~2.5-cm upstream of the outlet of the reactant inlet tube and 78 cm from the detection region. This allows sufficient distance (18 cm) for the helium flow to mix with the reactants and develop a parabolic velocity profile before reaching the reaction zone. Gas volumetric flow rates are determined with calibrated thermal conductivity type mass flowmeters. Flow speeds can be varied from 4 to 100 m s⁻¹. A calibrated MKS Baratron Model 310 capacitance manometer (0.8% accuracy) is used to measure pressure.

Alkali atoms are generated by heating the sample in a 2.5-cm-diameter cylindrical monel oven to a temperature commensurate with attaining a vapor pressure of that species of 10⁻⁴ to 10⁻⁶ torr within the oven. The oven is silver plated to resist alkali corrosion. The vapor is entrained in a flow of inert carrier gas and introduced into the flow tube through a 10-cm section of 19-mm o.d. silver tubing. The sodium vapor is further diluted by the carrier gas in the main flow tube so that the sodium concentration within the reaction zone is always less than 10⁻¹⁰ cm⁻³. For wall removal rate measurements the entire oven assembly may be placed downstream of the multi-channel arrays as a movable source. Since the oven is heated, it warms the main carrier gas flow slightly. Axial temperature surveys in the reaction region show that the final flow temperature profile is uniform at a value of 308 K.

Sodium hydroxide is produced via the reaction

$$Na + H_2O \rightarrow NaOH + OH \quad (6)$$

The partial pressure of H₂O₂ at 25 °C is 2.0 torr. Detection of NaOH is accomplished by converting it back to atomic sodium in the detection region, where the sodium is measured by laser-induced fluorescence (LIF). This conversion is accomplished by injecting an excess of atomic hydrogen into the flow 2-cm upstream of the LIF detector.

$$NaOH + H \rightarrow Na + H_2O \quad (7)$$

$$Na + h\nu \rightarrow Na^* \rightarrow Na + h\nu \quad LIF \text{ detection} \quad (8)$$

The hydrogen atoms, produced by microwave discharge of pure molecular hydrogen, are introduced through a 6-mm-diameter tube. With the mean flow velocity of 1000 cm s⁻¹, the reaction time of hydrogen in the detector (t₁) is 2 ms. The atomic hydrogen concentration is estimated to be \(2 \times 10^{12} \text{ cm}^{-3}\), by measuring the H₂ flow rate and assuming that 10% of the H₂ passing through the discharge dissociates, with no recombinaton or loss on the inlet tube walls. A Molecular DL14 nitrogen pumped dye laser is used for laser-induced fluorescence detection of Na. The laser-induced fluorescence data acquisition system and manipulation of data have been detailed elsewhere. However, it should be noted that fluorescence is usually averaged over 100 laser pulses, accounting for nonfluorescent background signals and for pulse-to-pulse fluctuations in laser intensity. The combined signal-to-noise ratio for these measurements generally exceeds 25.

The chemistries of the solutions used in these experiments are as follows: sodium metal, 99.995% (Alfa); helium, 99.995% (Northeast Cryogenics); hydrogen, 99.995% (Air Products); nitrogen, 99.999% (Northeast Cryogenics); and hydrogen chloride, 99.99% (Northeast Cryogenics). Hydrogen peroxide, obtained

$$(26) \text{ "JANAF Thermochemical Tables". The Dow Chemical Company. Midland, MI, 1970.}$$
$$(30) \text{ A. Fontijn and W. Felder, J. Phys. Chem., 83, 24 (1979).}$$

31kJmol⁻¹ <6)
One kinetic modeling program which numerically integrates the vacuum distillation. Titration with potassium permanganate as a 90% (by weight) solution from FMC Corp., is purified by Experimental Conditions.

Rate measurements are made with one reactant in excess of the other (detected) reactant, thus ensuring pseudo-first-order kinetic conditions. Reaction times are varied by changing the injector position of the flow tube. This is done with the Aerodyne PACKAGE and reaction in a flow tube. It assumes that Poiseuille flow exists for reaction rates determined by modeling the reactions occurring in a flow tube. It assumes that Poiseuille flow exists and provides ranges for k, k, (wall removal), and D (diffusion coefficient) for which the solutions have been shown to be valid. Wall removal rates of the species are determined in separate experiments by varying the oven position. The observed wall removal rate, as well as the reaction rate, is corrected for diffusion effects. Diffusion constants for alkali atoms and hydroxides were obtained from wall removal measurements in the instance where the observed disappearance of the species is diffusion limited.

An important aspect of the data analysis is the ability to ensure that secondary reactions have no effect on the concentration of the species being monitored. This could dramatically affect the accuracy of the rate measurements. The effects of secondary reactions are determined by modeling the reactions occurring in the flow tube. This is done with the Aerodyne PACKAGE code, a kinetic modeling program which numerically integrates the differential rate equations for a specified set of reactions. Backward reaction rates determined from the JANAF thermochemical tables and the forward rates are included, to ensure that accuracy is maintained.

Results

**Na + H₂O Reaction.** The NaOH formation rate was measured by directly observing the disappearance of sodium, with H₂O in known excess. The reaction has two exothermic product channels:

\[
\text{Na} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{OH}
\]

\[
\Delta H^o = -130 \pm 13 \text{ kJ mol}^{-1}
\]

\[
\text{Na} + \text{H}_2\text{O} \rightarrow \text{NaO} + \text{H}_2\text{O}
\]

\[
\Delta H^o = -130 \pm 42 \text{ kJ mol}^{-1}
\]

so what is measured by monitoring Na disappearance is the total reaction rate. However, one can add excess CO (≈ 2 × 10^{13} \text{ cm}^{-2}), which rapidly and quantitatively converts NaO to Na^{37}\text{Na}^{34}

\[
\text{NaO} + \text{CO} \rightarrow \text{Na}^{(37)\text{Na}} + \text{CO}_2
\]

\[
\Delta H^o = -259 \pm 42 \text{ kJ mol}^{-1}
\]

\[
\text{NaO} + \text{CO} \rightarrow \text{Na}^{(34)\text{Na}} + \text{CO}_2
\]

\[
\Delta H^o = -134 \pm 42 \text{ kJ mol}^{-1}
\]

Thus a measurement of the amounts of OH produced before and after addition of HCl provides the relative amounts of NaOH and NaO originally formed from Na + H₂O. The observed NaOH product fraction by this method is 0.60 ± 0.10, in excellent agreement with the value obtained from the rate measurements.

**NaO + HCl Reaction.** In the presence of excess O, the reaction of sodium with hydrogen peroxide produces only NaOH. With this reaction used as a source for NaOH, a series of rate measurements were made for the reaction of NaOH with HCl. First-order decays were linear for more than a factor of 10 in fluorescence signal, with the HCl concentrations ranging from 1 × 10^{-2} to 4 × 10^{-1} \text{ cm}^{-2}. The results of these experiments are shown in Figure 4, and the rate constant for this reaction is k = (6.9 ± 3.0) × 10^{-10} \text{ molecule}^{-1} \text{ s}^{-1}, and the fraction in the NaOH product channel is 0.61 ± 0.10. The major uncertainty in the rate constants k and k is the H₂O concentration, which is not directly measured but is obtained as indicated earlier.

An independent determination of the product branching ratio for reaction 6 is obtained by observing the hydroxyl radical via laser-induced fluorescence at 308.6 nm. When Na reacts with H₂O, only the NaOH product channel produces OH. However, when excess HCl is added to the NaO and NaOH product mixture, additional OH is formed by the reaction

\[
\text{NaO} + \text{HCl} \rightarrow \text{NaCl} + \text{OH}
\]

\[
\Delta H^o = -134 \pm 42 \text{ kJ mol}^{-1}
\]

Although the value for k_{10} has not been measured, indirect estimates from ref 37 imply k_{10} ≥ 10^{-11} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}. The large amount of CO added is required to ensure that all of the NaO cycles back to Na on a time scale much shorter than the reaction 6 to occur.

A rate measurement with CO present results in the production rate for only the NaOH branch. The results of these measurements are shown in Figure 3. Experimental conditions are given in Table 1. The reaction constant for both channels is k_{a} = (6.9 ± 3.0) × 10^{-10} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}, and the fraction in the NaOH product channel is 0.61 ± 0.10. The major uncertainty in the rate constants k and k is the H₂O concentration, which is not directly measured but is obtained as indicated earlier.

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---

**TABLE I: Typical Experimental Conditions**

<table>
<thead>
<tr>
<th>temp, K</th>
<th>flow velocity, m s⁻¹</th>
<th>press., torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>308</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>[Na], cm⁻³ (initial)</td>
<td>5 × 10⁻⁹</td>
<td></td>
</tr>
<tr>
<td>[H₂O], cm⁻³</td>
<td>1.3 × 10⁻³</td>
<td></td>
</tr>
<tr>
<td>[HCl], cm⁻³</td>
<td>(1-4) × 10⁻¹</td>
<td></td>
</tr>
<tr>
<td>[H], cm⁻¹</td>
<td>2 × 10⁻⁴</td>
<td></td>
</tr>
</tbody>
</table>

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(35) J. A. Silver, manuscript in preparation.
Gas-Phase Reaction of \( \text{NaOH} \) with \( \text{HCl} \)

**Figure 4.** First-order reaction rates vs. \([\text{HCl}]\) for the reactions of \( \text{NaOH} \) (\( \text{NaO} \)) + \( \text{HCl} \): (O) without \( \text{CO} \) added; (•) with \( \text{CO} \) added.

Separate measurements were also made without adding \( \text{CO} \). In this case \( \text{NaO} \), in addition to \( \text{NaOH} \), is present and reacts with \( \text{HCl} \) (reaction 11), complicating the analysis. Furthermore, the detection scheme, based on conversion to \( \text{Na} \) by addition of atomic hydrogen, would not appear to distinguish between \( \text{NaO} \) and \( \text{NaOH} \), since \( \text{Na} \) atoms are also produced in the reaction

\[
\text{NaO} + \text{H} \rightarrow \text{Na} + \text{OH} \tag{12}
\]

Thus, without \( \text{CO} \), the decrease in signal upon addition of \( \text{HCl} \) is due to both reactions 2 and 11, weighted by the branching ratio from reaction 6.6. The results, however, show the same decay with and without added \( \text{CO} \) (see Figure 4), implying that both \( \text{NaO} \) and \( \text{NaOH} \) react with \( \text{HCl} \) at approximately the same rate. This observation is reasonable if one considers the hydroxyl group on \( \text{NaOH} \) to act as a quasi-atom in respect to its chemical behavior given identical exothermicities for both reactions.

Separate \( \text{OH} \) measurements confirm that atomic hydrogen reacts with \( \text{NaO} \) as well as with pure \( \text{NaOH} \). Although we could not measure the \( \text{NaOH} \) + \( \text{HCl} \) rate constant directly, the observation that (1) \( \text{OH} \) is formed in the \( \text{NaOH} + \text{HCl} \) reaction (proving the existence of \( \text{NaO} \)), (2) \( \text{OH} \) is also formed upon addition of \( \text{HCl} \) to \( \text{NaOH} \), and (3) the decay rates with added \( \text{HCl} \) are identical both with or without \( \text{CO} \), imply that \( \text{NaO} \) reacts with \( \text{HCl} \) at approximately the same rate as \( \text{NaOH} \) with \( \text{HCl} \).

**Detector Corrections and Modeling.** Although the plots of \( \ln \) (signal) vs. reaction time are linear over the first order of magnitude decrease in signal, at longer times they flatten out at a value typically a few percent of the initial (zero reaction time) signal (Figure 5). This effect can be attributed to an additional component to the Na signal from the reaction

\[
\text{NaCl} + \text{H} \rightarrow \text{Na} + \text{HCl} \quad \Delta H^\circ = -21 \pm 2 \text{ kJ mol}^{-1} \tag{13}
\]

For the case with \( \text{CO} \) present, sodium formed in the detection region by addition of atomic hydrogen has two sources, \( \text{NaOH} \) and \( \text{NaCl} \); the amount of each depending on the extent to which the \( \text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} \) reaction has gone to completion. The rate equation for the formation of sodium in the detector is

\[
d[\text{Na}] = k_4[\text{NaOH}][\text{H}] + k_5[\text{NaCl}][\text{H}] \tag{14}
\]

**Figure 5.** Typical decay of fluorescence signal vs. reaction time for \( \text{NaOH} + \text{HCl} \), showing contribution to total detected sodium (---) from \( \text{NaOH} \) (----) and \( \text{NaCl} \) (-----). Circles are experimental data.

where the \( d \) subscript indicates the concentration at the entrance to the detector zone. Integrating over the detector reaction time (\( t_d \)), assuming excess hydrogen, we obtain

\[
[\text{Na}] = [\text{NaOH}]_0(1 - e^{4k[H]t_d}) + [\text{NaCl}]_0(1 - e^{-4k[H]t_d}) \tag{15}
\]

If no \( \text{HCl} \) is added, the observed LIF signal arises solely from \( \text{NaOH} \). We have observed that this signal (after correcting for differences in diffusion and wall removal between \( \text{Na} \) and \( \text{NaOH} \)) is identical with that arising from only sodium (i.e., without \( \text{H}_2\text{O}_2 \) added). This means that, within the available detector reaction time, all of the \( \text{NaOH} \) is converted to sodium, with an estimated error of 20%. This sets a lower limit to \( k_4[H]t_d \). Given \( t_d = 2 \) ms and \( [H] \approx 2 \times 10^{14} \text{ cm}^{-3} \), this requires that \( k_4 \geq 4 \times 10^{12} \text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1} \). The accuracy of \( t_d \) is ±0.5 ms. If less than 10% of the \( \text{H}_2 \) is dissociated (it is unlikely to be higher under our operating conditions), then \( k_4 \) is faster than the stated limit.

This value for \( k_4 \) is in reasonable agreement with a value of \( 1 \times 10^{17} \text{cm}^{-3}\text{s}^{-1} \) (1.7 \( \times \) \( 10^{11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 300 K) which is used by Hynes et al. in fitting their flame data over a wide range of conditions, and also with \( 2 \times 10^{17} \text{cm}^{-3}\text{s}^{-1} \) (1.4 \( \times \) \( 10^{12} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 300 K), which is used in various atmospheric models. The former value is claimed to be accurate to within a factor of two at flame temperatures, and the latter is only an estimate. We are planning to perform direct measurements of this reaction in the near future.

Now if we measure the reaction rate of \( \text{NaOH} + \text{HCl} \), at short reaction times the decay in signal is logarithmic because \( [\text{NaOH}]_0 \) \( > \) \( [\text{NaCl}]_0 \) and only the first term in eq 15 is significant. At long reaction times, \( [\text{NaCl}]_0 \geq [\text{NaOH}]_0 \) and the second term becomes dominant (Figure 5). If \( k_5 \approx k_4 \), we would never observe a decay in [Na] since both terms in eq 15 would always have the same sum. However, the fact that an initial decay is observed with a later leveling of signal shows that \( k_5 \ll k_4 \) and, from the relative value of the signal where it levels off, we can estimate \( k_5 \).

To determine \( k_5 \), we modeled this reaction system using the conditions in Table II and rate set in Table III. This rate set is more extensive than the above discussion implies because there could be secondary reactions between the excess \( \text{H}_2\text{O}_2 \) and the sodium formed in the detector, as well as other minor \( \text{OH} \), \( \text{H} \), and \( \text{CO} \) reactions.

**Table II.** Operating Conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>Present</td>
</tr>
<tr>
<td>NO</td>
<td>Present</td>
</tr>
<tr>
<td>H(_2)OH</td>
<td>Present</td>
</tr>
</tbody>
</table>

**Table III.** Rate Set

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na + HCl</td>
<td>( k_4 )</td>
</tr>
<tr>
<td>NaCl + H</td>
<td>( k_5 )</td>
</tr>
<tr>
<td>NaCl</td>
<td>( k_6 )</td>
</tr>
<tr>
<td>NaOH</td>
<td>( k_7 )</td>
</tr>
</tbody>
</table>

[1] This value is in reasonable agreement with a value of \( 1 \times 10^{17} \text{cm}^{-3}\text{s}^{-1} \) (1.7 \( \times \) \( 10^{11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 300 K) which is used by Hynes et al. in fitting their flame data over a wide range of conditions, and also with \( 2 \times 10^{17} \text{cm}^{-3}\text{s}^{-1} \) (1.4 \( \times \) \( 10^{12} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 300 K), which is used in various atmospheric models. The former value is claimed to be accurate to within a factor of two at flame temperatures, and the latter is only an estimate. We are planning to perform direct measurements of this reaction in the near future.
TABLE II: Initial Conditions Used in Chemical Model

<table>
<thead>
<tr>
<th>temp, K</th>
<th>308</th>
</tr>
</thead>
<tbody>
<tr>
<td>flow velocity, m s⁻¹</td>
<td>10.0</td>
</tr>
<tr>
<td>press., torr</td>
<td>2.0</td>
</tr>
<tr>
<td>[Na⁺] cm⁻³ (initial)</td>
<td>10⁶</td>
</tr>
<tr>
<td>[H₂O₂] cm⁻³</td>
<td>1.3 X 10³</td>
</tr>
<tr>
<td>[HCl] cm⁻³</td>
<td>1.93 X 10¹²</td>
</tr>
<tr>
<td>[H₂] cm⁻³</td>
<td>2 X 10⁻¹⁰ - 1 X 10⁻⁹</td>
</tr>
<tr>
<td>[H₂O] cm⁻³</td>
<td>10⁻¹⁰ - 10⁻¹¹</td>
</tr>
<tr>
<td>t, sec</td>
<td>0-25</td>
</tr>
<tr>
<td>t₀, sec</td>
<td>0-5.0</td>
</tr>
</tbody>
</table>

TABLE III: Reaction Rate Set Used for Modeling Na Chemistry

<table>
<thead>
<tr>
<th>reaction</th>
<th>k cm⁻³ molecule⁻¹ s⁻¹</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na + H₂O → NaOH + OH</td>
<td>6.9 X 10⁻¹²</td>
<td>b</td>
</tr>
<tr>
<td>NaOH + HCl → NaCl + H₂O</td>
<td>2.8 X 10⁻¹⁰</td>
<td>b</td>
</tr>
<tr>
<td>NaCl + H → Na + HCl</td>
<td>1.0 X 10⁻¹⁰</td>
<td>b</td>
</tr>
<tr>
<td>Na + H₂O → NaOH + O</td>
<td>1.0 X 10⁻¹⁰</td>
<td>est</td>
</tr>
<tr>
<td>2H₂O → 2O + 2H₂</td>
<td>1.6 X 10⁻¹²</td>
<td>39</td>
</tr>
<tr>
<td>O + H₂O → OH + H₂O</td>
<td>1.0 X 10⁻¹²</td>
<td>40</td>
</tr>
<tr>
<td>OH + H₂O → O₂ + HO₂</td>
<td>2.96 X 10⁻¹²</td>
<td>41</td>
</tr>
<tr>
<td>H + HO → H₂ + O</td>
<td>2.13 X 10⁻¹³</td>
<td>43</td>
</tr>
<tr>
<td>H + H₂O → OH + H₂O</td>
<td>2.76 X 10⁻¹³</td>
<td>42</td>
</tr>
<tr>
<td>H₂ + O → H + OH</td>
<td>7.7 X 10⁻¹³</td>
<td>40</td>
</tr>
<tr>
<td>O + H → OH + O</td>
<td>1.6 X 10⁻¹³</td>
<td>40</td>
</tr>
<tr>
<td>OH + H₂O → O₂ + H₂</td>
<td>8.0 X 10⁻¹⁰</td>
<td>40</td>
</tr>
<tr>
<td>H + O₂ → H₂ + O</td>
<td>3.2 X 10⁻¹¹</td>
<td>40</td>
</tr>
<tr>
<td>H + H₂O + O → H₂O₂ + O</td>
<td>1.4 X 10⁻¹¹</td>
<td>40</td>
</tr>
<tr>
<td>H + HO → H₂ + O</td>
<td>9.4 X 10⁻¹³</td>
<td>40</td>
</tr>
<tr>
<td>O + HO → O₂ + H</td>
<td>8.0 X 10⁻¹¹</td>
<td>40</td>
</tr>
<tr>
<td>2OH → O + H₂O</td>
<td>1.8 X 10⁻¹²</td>
<td>40</td>
</tr>
<tr>
<td>HCl + OH → H₂O + Cl</td>
<td>6.6 X 10⁻¹³</td>
<td>40</td>
</tr>
</tbody>
</table>

No three-body rates were used because the system is at low pressure. This work.

etc. reactions. This model also includes the undissociated hydrogen, and the water impurity (~7%) in the H₂O₂. We systematically varied $k_p$, $k_{13}$, [H], [H₂O₂], and $r$. The results show that all secondary reactions have little effect (~6%) on the calculated sodium densities and that the variations of Na with [H₂O₂] and [H₂] are small, in reasonable agreement with additional experiments. The value for $k_{13}$, which best fits the experimental data is (8 ± 3)/(H), which leads to $k_{13}$ in the range $1 \times 10^{-12}$ to $5 \times 10^{-14}$ cm molecule⁻¹ s⁻¹, with a best estimate of $5 \times 10^{-14}$ cm molecule⁻¹ s⁻¹. In light of the small exothermicity for this reaction, this value is not unreasonable. If the rate constant is expressed in the Arrhenius form: $k = A e^{-E/R}$, this would correspond to only a 21 kJ mol⁻¹ barrier, even with a gas kinetic preexponential term.

Discussion

The reaction rate constant of HCl with NaOH is found to be in its gas kinetic limit. This is a consequence of obvious steric effects, and the fact that reactant and product energies are comparable. The reaction rate constant $k$ is in the range estimated by Rowland and Rogers, and the partitioning of total sodium among NaOH, NaO, and NaO₂ is on the order of 5 x 10⁻¹⁰ cm⁻³. If all of the meteoric sodium were in the form of NaOH at 40 km, our measurement of $k$ would give a first-order rate constant for Cl formation of $1.4 \times 10^{-6} \text{s}^{-1}$, providing that $\Delta G_{cl}$ is in the range estimated by Rowland and Rogers. This is a factor of ~20 faster than the first-order rate constant for Cl regeneration from OH + HCl of $6 \times 10^{-10} \text{s}^{-1}$, based on an OH concentration of $10^{-11} \text{cm}^{-3}$ and the value $k_{2}(250 \text{K}) = 5.7 \times 10^{-10} \text{cm}^{-3} \text{molecule}^{-1} \text{s}^{-1}$. Although the partitioning of total sodium among NaOH, NaO, and NaO₂ requires a more detailed knowledge of rate constants for the processes shown in Figure 1, this calculation demonstrates that, even if only 5% is in the form of NaOH, regeneration of Cl from HCl via alkali chemistry would be comparable to regeneration by the OH reaction.

This simple computation leads us to two conclusions: First, our results for this and the other alkali reactions described show that meteoric metal reactions may have a potentially significant impact on our understanding of chemistry in the mesosphere and upper stratosphere. The large values of the sodium rate constants measured in this study emphasize this possibility. Secondly, it clearly motivates the need for further investigation of these phenomena.


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Acknowledgment. The authors thank Drs. F. Kaufman, M. McElroy, and E. Murad for their helpful discussions and insights.
SECTION 5

GAS-PHASE REACTION RATE OF SODIUM SUPEROXIDE WITH HYDROCHLORIC ACID

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Prepared for
Journal of Physical Chemistry

October 1985

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GAS-PHASE REACTION RATE OF SODIUM SUPEROXIDE WITH HYDROCHLORIC ACID

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ABSTRACT

Metal compounds originating from meteor ablation may be an additional mechanism for the release of free chlorine from HCl in the stratosphere. For the alkali metals, and sodium in particular, catalytic chemical pathways have been postulated which describe these processes. A critical step in this mechanism is the reaction of NaO2 with HCl. We have measured the rate constant for this reaction in a fast-flow reactor at 295 K and find it to be $(2.3 \pm 0.4) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The implication of this result on stratospheric ozone chemistry is discussed.

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INTRODUCTION

In the past few years, a number of experimental rate constant measurements have been completed\textsuperscript{1-5} which support the contention that alkali metals originating from meteor ablation may have a significant role in determining the extent to which ozone might be depleted by chlorine compounds in the upper stratosphere.\textsuperscript{6-7} This would be accomplished by the sodium catalyzed release of free chlorine from the inactive HCl stratospheric reservoir at a rate comparable to the major recognized reaction

\[
\text{HCl} + \text{OH} + \text{Cl} + \text{H}_2\text{O} \quad (1)
\]

The chemistry of alkali metals in the lower thermosphere and upper stratosphere has been discussed elsewhere,\textsuperscript{1,8-14} and will only be highlighted here. Metals (in particular, sodium) volatilized during meteor entry into the earth's atmosphere are oxidized and enter the upper stratosphere as a mixture of NaO\textsubscript{2}, NaO, and NaOH. The suggested catalytic cycle for release of free chlorine comes as a result of the reaction of these species with HCl, and their subsequent regeneration on a time scale comparable to that of reaction 1.
NaO₂ + HCl + NaCl + H₂O  \hspace{1cm} (2)
NaO + HCl + NaCl + OH  \hspace{1cm} (3)
NaOH + HCl + NaCl + H₂O  \hspace{1cm} (4)
NaCl + H⁺ + Na + Cl  \hspace{1cm} (5)
Na + O₂ + \text{NaO₂}  \hspace{1cm} (6)
NaO₂ + (O, OH, H, etc)\ldots + \text{NaOH, NaO}  \hspace{1cm} (7)

Recent kinetic measurements on reactions 3, 4, and 6 indicate that these proceed rapidly.¹⁻⁴ Estimates of the photolysis rates of NaCl,⁷ based on high temperature absorption cross section measurements,¹⁵ are also relatively fast (10⁻² - 10⁻³ s⁻¹), so that the potential rate limiting step(s) to this process is the conversion of NaO₂ to NaCl, either directly through reaction 2, or indirectly via step 7 and reactions 3 and 4. If the overall rate constant for Cl formation of either of these is comparable to that for reaction 1 (k₁[OH] = 10⁻⁶ s⁻¹), then the presence of alkali metals may indeed impact stratospheric ozone levels.

The purpose of this study is to provide a measurement of the rate constant for the direct path, i.e., the reaction of NaO₂ + HCl + NaCl + H₂O. The results of this measurement should help confirm whether or not meteoric metals could play a significant role in stratospheric ozone chemistry.
EXPERIMENTAL SECTION

The fast-flow reactor and experimental techniques used in these experiments have been fully described in previous papers.\textsuperscript{1,16} Briefly, the flow reactor is a 7.26-cm-diameter, 120-cm-long alumina tube with four perpendicular side arms at the tube exit which permit optical detection of the reactive species. Helium carrier gas is added at the entrance of the flow tube through mullite multichannel arrays which laminarize the flow. Gas volumetric flow rates are determined with calibrated thermal conductivity type mass flow meters. Flow rates of hydrogen chloride are determined by diverting the flow into a calibrated volume, and then measuring the rate of pressure increase. A calibrated MKS Baratron Model 310-BSH10 capacitance manometer (0.8\% accuracy) is used to measure pressure.

Sodium atoms are generated by heating the sample in a 2.5-cm-diameter cylindrical monel oven to a temperature commensurate with attaining a vapor pressure of that species of $10^{-6}$ to $10^{-4}$ torr within the oven. The oven is enclosed in a 4-cm-diameter water-cooled sheath to prevent heating of the main flow carrier gas. The vapor is entrained in a flow of inert carrier gas and introduced directly into the flow tube. The sodium vapor is further diluted by the carrier gas in the main flow tube so that the sodium concentration within the reaction zone is always less than $10^{10}$ cm$^{-3}$.

Sodium superoxide is produced via the termolecular reaction

\[
Na + O_2 + M + NaO_2 + M ,
\]

(6)
where $M = \text{He}$ and $k_6(\text{He}) = 1.4 \times 10^{-30} \text{ cm}^6 \text{s}^{-1}$ at 295 K. Molecular oxygen ($\sim 10^{15} \text{ cm}^{-3}$) is added to the carrier gas in the flow tube and reacts rapidly under the conditions present (2.07 torr, 295 K), so that conversion of Na to NaO$_2$ is essentially complete before reaching the region where HCl is injected into the flow.

Detection of NaO$_2$ is accomplished by converting it back to atomic sodium in the detection region, where it is measured by resonance fluorescence. This conversion is done by injecting an excess of atomic hydrogen into the flow 2-cm upstream of the detection volume.

\[
\text{NaO}_2 + \text{H} + \text{Na} + \text{H}_2 \text{O} \rightarrow \text{Na} + \text{H}_2 + \text{Na} + \text{H}_2 \text{O} \quad \Delta H_r = 39 \pm 20 \text{ kJ mol}^{-1} \quad (8)
\]

\[
\text{Na} + \nu \rightarrow \text{Na}^* + \text{Na} + \nu \quad \text{(resonance fluorescence)} \quad (9)
\]

The hydrogen atoms, produced by microwave discharge of pure molecular hydrogen, are introduced through a 6-mm-diameter quartz tube, whose inner walls are coated with syrupy phosphoric acid. With the mean flow velocity of 920 cm s$^{-1}$, the reaction time of hydrogen in the detector ($t_d$) is ~2 ms. The atomic hydrogen concentration is estimated to be $2 \times 10^{14} \text{ cm}^{-3}$, by measuring the H$_2$ flow rate and assuming that 10% of the H$_2$ passing through the discharge dissociates, with no recombination$^{17}$ or loss on the inlet tube walls.$^{18}$

5-6
Resonance fluorescence is accomplished using a 25-Watt Spectroline sodium resonance lamp and phase-sensitive detection techniques. The data are fed directly into an IBM/XT computer for processing. Purities of the chemicals used in these experiments are as follows: sodium metal, 99.95% (Alfa); helium, 99.995% (Northeast Cryogenics); oxygen 99.993% (Northeast Cryogenics); hydrogen, 99.995% (Air Products); and hydrogen chloride 99.99% (Northeast Cryogenics).

Rate measurements are made with $[\text{HCl}] > [\text{NaO}_2]$, thus ensuring pseudo-first-order kinetic conditions. Reaction times were varied from 1 to 15 ms by changing the injector position. Data analysis and corrections for wall loss and diffusion effects were performed as described in our previous work on the reactions of NaO and NaOH with HCl\textsuperscript{1,19} The diffusion coefficient for NaO\textsubscript{2} in helium was estimated to be 0.3 cm\textsuperscript{2} s\textsuperscript{-1} at 1 atm, but in fact, the correction for diffusion was quite insensitive to this value (i.e., less than one percent difference if 0.4 cm\textsuperscript{2} s\textsuperscript{-1} was used).

**RESULTS**

Decay of NaO\textsubscript{2} for seven concentrations of HCl covering the range 1.02 - 41.9 x 10\textsuperscript{11} cm\textsuperscript{-3} are shown in Figure 1. The first order decay rates obtained from the slopes of these lines and corrected for diffusion effects are plotted versus the corresponding HCl concentration in Figure 2. A least-squares fit to the slope of this line, weighted by the uncertainties in each point, results in a value of the rate constant for this reaction of $(2.3 \pm 0.4) \times 10\textsuperscript{-10}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}. The uncertainty expressed in this expression
includes precision errors (one standard deviation), as well as estimated 
errors in accuracy.

In previous measurements of this type, corrections to the data were 
required to account for the reaction of NaCl product with the atomic hydrogen 
titrant,

\[ \text{NaCl} + \text{H} + \text{Na} + \text{HCl} \]  

We had estimated the rate constant for this reaction as \( -5 \times 10^{-14} \pm 1 \) 
cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). In these experiments, the decays were observed for 
reaction times varying between one and fifteen milliseconds, and under these 
conditions, reaction 10 has insufficient time to proceed enough to require any 
data corrections.

**DISCUSSION**

Similar to NaO and NaOH, NaO\(_2\) reacts with HCl with a rate constant near 
its gas kinetic limit. Although the first two reactions are considerably 
exothermic (133 $\pm$ 13 kJ mole\(^{-1}\) and 134 $\pm$ 42 kJ mole\(^{-1}\), respectively), the last 
is most probably barely exothermic by 19 $\pm$ 21 kJ mole\(^{-1}\). Since the NaO\(_2\) bond 
is strongly ionic,\(^{20}\) one might explain its reactivity with HCl in a manner 
similar to that given for NaOH and NaO,\(^{1}\) for the alkaline earth dihalides with 
Cl\(_2\) and HCl,\(^{21}\) and for cesium halides with Cl\(_2\) and ICl.\(^{22}\) In all of these 
examples, large dipole-dipole and dipole-induced dipole interactions provide 
strong long-range forces which lead to the formation of an ion-pair adduct, 
allowing a facile exchange reaction. In this case the adduct would likely be
Na\textsuperscript{+}(HOOC\textsubscript{1})\textsuperscript{−}. Although the (HOOC\textsubscript{1})\textsuperscript{−} species has not been observed, it is analogous to the (HOOH)\textsuperscript{−} ion, which has indirectly been shown to exist, although its exact structure is unknown.\textsuperscript{23}

Demonstration of a nearly gas kinetic reaction rate constant for Na\textsubscript{2}H\textsubscript{1} + H\textsubscript{1}Cl supports the possibility that a sodium catalyzed Cl regeneration mechanism can be fast enough to compete with the OH + H\textsubscript{1}Cl reaction in the upper stratosphere. Estimates of total stratospheric sodium concentrations by Liu and Reid\textsuperscript{24} are on the order of 5 x 10\textsuperscript{5} cm\textsuperscript{−3}. If most of the sodium is in the form of NaOH, NaO\textsubscript{2}, or NaO, then the measured rate constants for reactions 2-4 result in a first-order rate constant for Cl release of \(-1 \times 10^{-4}\) s\textsuperscript{−1}, much larger than the 10\textsuperscript{−6} s\textsuperscript{−1} required for competition with reaction 1. Given the results of this work, and a recent study of room temperature NaCl photolysis rates,\textsuperscript{25} the rate limiting step for the mechanism given by reactions 2-7 may be the photolysis of NaCl, so that it is probable that only \(-1-10\%\) of the daytime molecular sodium is in the above molecular forms. Even at this level, this Cl release mechanism could be competitive with reaction 1.

One must also consider both homogeneous and heterogeneous loss mechanisms for gas phase alkali, which are all poorly understood. Homogeneous losses could include NaCl polymerization\textsuperscript{26} and ionization/cluster formation,\textsuperscript{27} while heterogeneous losses might include condensation onto small particulates\textsuperscript{28} or liquid droplets at lower altitudes. The degree of alkali loss at the present time is uncertain, but if only 10\% of the stratospheric alkali is left unscavenged, then the catalytic release of free chlorine by ablated meteor metals could still be significant on the upper stratospheric ozone balance.
ACKNOWLEDGEMENTS

The authors gratefully acknowledge the many insightful discussions with and the contributions of the late Dr. Fred Kaufman, and will miss him greatly. This work was supported by the Fluorocarbon Program Panel of the Chemical Manufacturers Association under Contract No. FC-84-494 and the Air Force Geophysics Laboratory under Contract No. F19628-83-C-0010, and the Army Research Office under Contract No. DAAG 29-81-C-0024.
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Gozewski, S. Kallelis, and J.C. Wormhoudt, Rev. Sci. Instrum., 1981, 52,
1213.
1976, 65, 4739.
FIGURE CAPTIONS

Figure 1. Pseudo-first-order decays for NaO$_2$ + HCl reaction.

\[ [\text{HCl}] = 1.02 ( \bigcirc ), 9.21 ( \bullet ), 12.6 ( \square ), 17.0 ( \blacksquare ), 20.9 ( \triangle ), \\
35.5 ( \blacktriangle ), 41.9 ( \diamond ); \text{ units of } 10^{11} \text{ molecules cm}^{-3} \]

Figure 2. Dependence of corrected pseudo-first-order rate constant on HCl concentration at 295 K.
RELATIVE SIGNAL vs. REACTION TIME (msec)
NaO₂ + HCl → NaCl + HO₂

\[ k^1(\text{sec}^{-1}) \]

\[ [\text{HCl}] \ (10^{12} \text{ molecules cm}^{-3}) \]

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SECTION 6

ABSOLUTE PHOTODISSOCIATION CROSS SECTIONS OF GAS-PHASE SODIUM CHLORIDE AT ROOM TEMPERATURE

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ABSTRACT

Absolute photodissociation cross sections for gas phase NaCl are measured over the wavelength range of 189.7 to 359.8 nm at 300 K. Two well-resolved peaks are observed at 235 nm and 260 nm. The cross section also rises below 210 nm. These results are in good qualitative agreement with previous high temperature measurements and with cross sections computed from theoretically calculated potential surfaces. However, there are two significant differences, the width of the absorption peaks and to absolute magnitude of the cross sections. The importance of these measurements in understanding the photodissociative processes of ionic compounds and the implications for the role of NaCl in the stratospheric chemistry of chlorine compounds are discussed.

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INTRODUCTION

The study of the optical spectra of gas phase alkali halides has a long and rich history,\textsuperscript{1} having been pursued in flames,\textsuperscript{2–3} furnaces,\textsuperscript{4} shock tubes,\textsuperscript{5} and more recently, in room temperature cells\textsuperscript{6} and molecular beams.\textsuperscript{3,7–11} In conjunction with these experimental studies, the theory of photodissociation of alkali halides has received considerable attention.\textsuperscript{1,12–14}

Photodissociative processes for these systems are often approximated as one-electron charge transfers between a ground ionic state and excited covalent state. Measurement of the spectrally-resolved cross sections and determination of the relative probability of exciting parallel ($0^+ + \Sigma^+$) and perpendicular ($1 + \Sigma^+$) transitions lead to information about the shapes of the excited state potentials. Combined with product analysis, one can then learn how dissociation from the $0^+$ excited states is affected by the degree of adiabatic behavior in the exit channel when crossing the ionic $\Sigma^+$ potential curve.

The measurement of photodissociation cross section is also of interest in understanding the chemistry of alkali metals in the stratosphere. It has been suggested\textsuperscript{15–17} that sodium and other metals introduced into the atmosphere by meteor ablation may play a role in affecting ozone reduction by the catalytic chlorine cycle. One possible reaction sequence which demonstrates this mechanism is:

\begin{align*}
Na + O_2 + M &\rightarrow NaO_2 + M , \quad (1) \\
NaO_2 + HCl &\rightarrow NaCl + HO_2 , \quad (2)
\end{align*}
\[ \text{NaCl} + \text{hv} \rightarrow \text{Na} + \text{Cl}, \]  
\[ \text{(3)} \]

which leads to the net reaction

\[ \text{HCl} + \text{O}_2 + \text{hv} \rightarrow \text{Cl} + \text{HO}_2, \]  
\[ \text{(4)} \]

Rate constants for reactions 1 and 2 have been measured in our laboratory.\textsuperscript{18-19} Combining these results with photolysis rates based on the high temperature absorption measurements (1123-1223 K) of Davidovits and Brodhead,\textsuperscript{9,17} leads to the possibility that this mechanism could be comparable in magnitude to the major stratospheric Cl regeneration mechanism,

\[ \text{OH} + \text{HCl} + \text{Cl} + \text{H}_2\text{O}, \]  
\[ \text{(5)} \]

The rate limiting step of the sodium catalyzed mechanism (reactions 1-3) is reaction 3. Davidovits' absorption data include contributions from vibrationally excited states and possibly dimers, which will not contribute to photolysis at stratospheric temperatures near 260 K. Clearly, low temperature photodissociation cross section measurements are desirable.

In this paper we report measurements of the absolute cross section for photodissociation of NaCl at 300 K. Sodium chloride is produced by the gas phase reaction of atomic sodium with chlorine in a flow tube under dimer-free conditions and with over 80% of the NaCl in the ground vibrational state. The approach taken in these experiments does not require the knowledge of the absolute NaCl number density in the photolysis region, but rather uses a ratio technique to quantify the cross sections.
EXPERIMENTAL

Photodissociation Apparatus

Sodium chloride is generated in a flow tube by the fast bimolecular reaction of atomic sodium with excess chlorine,

\[ \text{Na} + \text{Cl}_2 \rightarrow \text{NaCl} + \text{Cl} \]  \[ k = 6.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]  \( \text{(6)} \)

Sodium atoms are generated by heating sodium metal in a 2-cm-diameter cylindrical stainless steel oven to 510 K which produces a vapor pressure of \(2 \times 10^{-3} \text{ torr}\) within the oven. The vapor is entrained in a flow of helium, and carried through a heated 0.6-cm-diameter 40-cm-long stainless steel tube into the flow apparatus. This heated tube is wrapped with \(-0.3\)-cm-thick zirconia blanket insulation and enclosed in a water cooled jacket to prevent any heating of the main flow carrier gas. The sodium vapor is diluted by the carrier gas in the main flow so that the sodium or sodium chloride concentration within the photolysis zone is always less than \(10^{10} \text{ cm}^{-3}\). Chlorine is mixed with the main carrier flow and its reaction with sodium is complete within a few centimeters of the sodium inlet orifice.

The flow apparatus is comprised of a small stainless steel tube 9.7 cm in diameter and approximately 50 cm long, with four perpendicular side arms at
the detection zone which permit photodissociation and detection of the flow species (Figure 1). The main flow of helium carrier gas is added at the entrance of the flow tube and a small purge flow of helium is introduced in each of the side arms to keep the optics clean. Gas volumetric flow rates are determined with calibrated thermal conductivity-type mass flow meters. Flow rates of chlorine are determined by diverting the flow into a calibrated volume and measuring the rate of pressure increase. A calibrated MKS Baratron capacitance manometer is used to measure pressure and a chromel-alumel thermocouple is used to determine the gas temperature. Experiments are performed with a flow velocity of 150 cm s\(^{-1}\) at a pressure of 2.1 torr.

Relative concentrations of atomic sodium are measured using laser-induced fluorescence of the 3s\(^2\)S\(_{1/2}\) - 3s\(^2\)P\(_{3/2}\) transition at 589.9 nm. The output of a nitrogen-pumped dye laser (Molectron DL14) is transmitted to the experiment by a fiber optic line and is focussed in the photolysis region to a diameter of 0.380 ± 0.005 cm. Fluorescence is detected by a photomultiplier located perpendicular to the laser path as shown in Figure 1. A 590 nm interference filter and optical baffles are used to reject spurious light from entering the PMT. A 1 cm diameter area of the photolysis region is imaged onto the phototube. The data are collected using a fast preamplifier and a gated integrator having a 60 ns acquisition gate width. The relative laser power in each pulse is monitored by a fast photodiode and is integrated and held until both the laser power and fluorescence signals are read into an IBM PC/XT computer for analysis.
Sodium chloride is photodissociated with a Raman-shifted excimer laser. The excimer laser (Questek) is equipped with unstable resonator optics and produces a beam with very low divergence. It uses either ArF or KrF with output pulse energies of 100-250 mJ. Its output is reflected by a dielectric-coated mirror into a Quanta Ray RS-1 Raman shifter. Using D$_2$, H$_2$, or a mixture of the two, both Stokes and anti-Stokes shifted wavelengths of the pump line are produced with pulse energies in the range 0.0023-4.4 mJ.

This UV beam is focused into the cell coaxial to the dye laser beam, with care taken to ensure that the UV beam diameter is equal to or slightly less than that of the dye laser. A BK-7 window (F1 in Figure 1) on the UV output side of the cell (visible input side) is used to absorb the UV light so that it cannot be refocused into the fiber optic or interfere with the visible power measurements. A calibrated Scientech power meter is used to monitor the average UV power as it exits the photolysis cell. Corrections are made for transmittance of the output window and spectral response of the power monitor.

Triggering of both lasers and the time delay between them (variable from 0-10 ms in 10 ns increments) is controlled by a delay generator. The excimer is triggered at a frequency (30 Hz) twice that of the dye laser, so that any non-photodissociation related components of the signal are subtracted from the fluorescence of photodissociated sodium. The data acquisition system performs both these subtractions of background signals as well as normalization of the fluorescence to the power of each visible laser pulse. It then averages the corrected signals over a minimum of 100 pulses.
The purities of chemicals used in these experiments are as follows:
sodium metal, 99.9% (Alfa); helium, 99.995% (Northeast Cryogenics); and
chlorine, 99.5% (Northeast Cryogenics).

Experimental Procedure and Data Analysis

Photodissociation cross sections are measured using a probe-pump-probe
approach. The first step consists of measuring the atomic sodium
concentration with no chlorine present, \([\text{Na}]_0\), in the photolysis region
using the visible dye laser. Excess molecular chlorine is then added at the
upstream end of the flow tube, quantitatively converting all of the Na to NaCl
in a distance much shorter than the 17 cm path between the sodium oven outlet
and the photolysis region. The NaCl is then photodissociated with the UV
laser and the product sodium \([\text{Na}]_p\) detected with the visible laser
approximately 200 ns later. This signal is related to the initial
concentration of NaCl by

\[
\frac{[\text{Na}]_p}{[\text{NaCl}]} = 1 - \exp[-I(\lambda)\sigma(\lambda)]
\]  

(7)

where \(I(\lambda)\) is the ultraviolet laser photon fluence per pulse at wavelength \(\lambda\),
and \(\sigma(\lambda)\) is the photodissociation cross section at this wavelength. Because
\([\text{NaCl}]= [\text{Na}]_0\), we rewrite equation 7,

\[
R = \frac{[\text{Na}]_p}{[\text{Na}]_0} = 1 - \exp[-I(\lambda)\sigma(\lambda)]
\]  

(8)
Since the detection techniques for measuring atomic sodium before and after the photolysis are identical, the ratio of their absolute concentrations in equation 8, defined as \( R \), is equivalent to the ratio of their observed fluorescence signals. As a result, only \( I(\lambda) \) need be measured absolutely.

This determination of \( \sigma(\lambda) \) requires a few assumptions and clarifications. Since \( R \) depends exponentially on the UV photon flux, nonuniformities could introduce errors when using the spatially-averaged value of \( I(\lambda) \). This is avoided by keeping the UV beam intensity low enough so that \( R \) is always less than 0.05. Accordingly, the exponential term can be expanded and rewritten as

\[
\sigma(\lambda) = \frac{R}{I(\lambda)}
\]

(9)

In this situation, \( R \) is linearly proportional to \( I(\lambda) \), and the spatially-averaged value of \( R \) is independent of any intensity nonuniformities. We confirmed the linearity of the cross section by measuring \( R \) as a function of laser intensity for some of the more intense UV lines. A linear dependence of \( R \) on \( I(\lambda) \) was observed at lower intensities, becoming nonlinear at the highest intensities. We always operated in the linear regime. The intensity profile of the visible laser beam is kept uniform to avoid nonlinearities in \( R \).

The time delay between lasers is also critical. It must be small enough so that all of the sodium formed by dissociation is detected before reacting.
with the remaining Cl\textsubscript{2}. To detect at least 98% of this sodium, and with Cl\textsubscript{2} concentrations on the order of 0.4-1.0 \times 10^{13} \text{cm}^3, (large enough to react with Na in a distance much shorter than the distance from the oven to the photolysis region) the laser delay should be less than 3.0 \mu s. On this time scale, the recoiling of photodissociated sodium will be thermalized. We measured the decrease in [Na]\textsubscript{p} as a function of delay time and observe a decay (τ \approx 100 \mu s) commensurate with this secondary reaction with Cl\textsubscript{2} and with diffusion out of the detection region. On the other hand, it is desirable to have some delay so as to avoid any electronic interference or UV induced effects associated with the excimer pulse. Thus delays between 200 ns and 2.0 \mu s were used.

The most significant correction to the data arises in accounting for the different diffusivities of Na and NaCl. As mentioned above, Na emanating from the oven travels ~17 cm before being detected. When quantitatively converted to NaCl (in 1-2 cm), the NaCl then travels ~15 cm before detection. In our initial analysis above we have assumed that [NaCl] = [Na]\textsubscript{0} in the photolysis region. However, this is only approximately correct. Although true at the end of the narrow reaction zone, these species' axial concentrations will decay at different rates due to diffusion to and sticking on the reactor walls. A correction must therefore be made for the differing diffusivities of Na and NaCl. This is done according to the methods outlined in reference 21, using a measured diffusion coefficient for atomic sodium of 0.48 cm\textsuperscript{2} s\textsuperscript{-1} at 1 atm and 300 K, and an approximate value for NaCl of 0.40±0.05 cm\textsuperscript{2} s\textsuperscript{-1} at 1 atm.\textsuperscript{22} The underestimation of [NaCl] in the photolysis region results in a reduction in R by a factor of 1.4±0.4. This
systematic error affects only the absolute magnitude of the photodissociation cross section curve as a function of wavelength, but not the relative shape of the curve.

RESULTS

Room temperature photodissociation cross sections for gaseous NaCl were measured at 25 wavelengths in the range 189.9-359.8 nm. A plot of the results is shown in Figure 2. Error bars represent one standard deviation uncertainties in each point, excluding a systematic error of ±30% due to the correction for diffusion. This last uncertainty would have the effect of uniformly shifting the curve up or down. Table 1 lists the averaged data taken at each wavelength and illustrates the ability of this technique to accurately measure very small cross sections. Our results exhibit two distinct peaks and a rise in $\sigma$ toward the shortest wavelengths. We do not observe any dissociation at energies below $100 \text{ kcal mole}^{-1}$ (285 nm), which is consistent with the currently accepted value for the bond strength of $98\pm2$ kcal mole$^{-1}$.$^9,23$

As seen in Figure 2, the error bars for most points are less than 20%, except (unfortunately) at the center of the large peak at 234 nm. This point and the next two higher wavelength points were taken using very weak Raman-shifted lines (the latter two being combinations of Stokes and anti-Stokes lines),$^{24}$ so that there is a greater uncertainty in the absolute height of this peak as compared with the longer wavelength peak. For most points, the source of the error bars lies in the absolute UV power measurement and not in the determination of the ratio of $[\text{Na}]_p/[\text{Na}]_0$. 

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Table 1 - Measured Photodissociation Cross Sections for NaCl

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Excimer Gas</th>
<th>Raman-Shifted Line&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Number of Measurements</th>
<th>Avg. Cross Section&lt;sup&gt;b&lt;/sup&gt; (cm&lt;sup&gt;2&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>189.7</td>
<td>KrF</td>
<td>AS&lt;sub&gt;3&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>2</td>
<td>6.12±1.44 (-18)</td>
</tr>
<tr>
<td>193.4</td>
<td>ArF</td>
<td>-</td>
<td>4</td>
<td>5.56±1.06 (-18)</td>
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<td>203.1</td>
<td>KrF</td>
<td>AS&lt;sub&gt;3&lt;/sub&gt;(D&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>1</td>
<td>1.48±1.40 (-18)</td>
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<tr>
<td>205.3</td>
<td>ArF</td>
<td>S&lt;sub&gt;1&lt;/sub&gt;(D&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>2</td>
<td>9.06±1.48 (-19)</td>
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<tr>
<td>205.9</td>
<td>KrF</td>
<td>AS&lt;sub&gt;2&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>1</td>
<td>8.96±0.60 (-19)</td>
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<tr>
<td>210.3</td>
<td>ArF</td>
<td>S&lt;sub&gt;1&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>2</td>
<td>7.36±0.59 (-19)</td>
</tr>
<tr>
<td>216.3</td>
<td>KrF</td>
<td>AS&lt;sub&gt;2&lt;/sub&gt;(D&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>1</td>
<td>1.51±0.67 (-18)</td>
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<td>218.7</td>
<td>ArF</td>
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<td>2</td>
<td>4.63±1.76 (-19)</td>
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<td>4</td>
<td>1.46±0.08 (-18)</td>
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<tr>
<td>230.4</td>
<td>ArF</td>
<td>S&lt;sub&gt;2&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>3</td>
<td>5.12±0.40 (-18)</td>
</tr>
<tr>
<td>231.2</td>
<td>KrF</td>
<td>AS&lt;sub&gt;1&lt;/sub&gt;(D&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>2</td>
<td>9.47±0.80 (-18)</td>
</tr>
<tr>
<td>234.0</td>
<td>ArF</td>
<td>S&lt;sub&gt;3&lt;/sub&gt;(D&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>2</td>
<td>1.30±0.30 (-17)</td>
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<td>237.6</td>
<td>KrF</td>
<td>S&lt;sub&gt;1&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;)+AS&lt;sub&gt;2&lt;/sub&gt;(D&lt;sub&gt;2&lt;/sub&gt;)&lt;sup&gt;c&lt;/sup&gt;</td>
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<tr>
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<td>1</td>
<td>2.51±1.19 (-18)</td>
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<tr>
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<td>3</td>
<td>4.24±0.41 (-18)</td>
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<tr>
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<td>KrF</td>
<td>AS&lt;sub&gt;1&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;)+S&lt;sub&gt;2&lt;/sub&gt;(D&lt;sub&gt;2&lt;/sub&gt;)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1</td>
<td>4.33±1.50 (-18)</td>
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<td>KrF</td>
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<td>4</td>
<td>1.74±0.23 (-18)</td>
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<tr>
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<td>KrF</td>
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<td>6</td>
<td>4.00±0.47 (-19)</td>
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<td>285.0</td>
<td>ArF</td>
<td>S&lt;sub&gt;4&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>2</td>
<td>0 ±1.8 (-19)</td>
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<td>291.8</td>
<td>KrF</td>
<td>S&lt;sub&gt;2&lt;/sub&gt;(D&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>2</td>
<td>8 ±1 (-21)</td>
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<td>0 ±9 (-21)</td>
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<tr>
<td>359.8</td>
<td>KrF</td>
<td>S&lt;sub&gt;3&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>1</td>
<td>2.7±3.1 (-21)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Designation of Stokes or anti-Stokes line with gas used in the Raman-shift cell in parentheses. Gas cell pressures were 125 psig for H<sub>2</sub> and 250 psig for D<sub>2</sub>.

<sup>b</sup> Exponent in parentheses; error is one standard deviation uncertainty in precision.

<sup>c</sup> These are combination Raman-shift lines in a 25% H<sub>2</sub>:75% D<sub>2</sub> mixture at 250 psig total pressure.
DISCUSSION

The results presented in this work are in qualitative agreement with the earlier work of Davidovits and Brodhead. However, there are two significant differences: the resolution of the absorption peaks and the absolute magnitude of the cross sections. Gaseous alkali halides in the earlier work were produced in a heated reservoir and effused into a slightly warmer quartz absorption cell. For NaCl, cell temperatures were in the range of 1123-1223 K. At these temperatures, the first five vibrational levels account for over 90% of the population. One might expect broad absorption features since each excited vibrational state will dissociate over a different range of energies than for the ground vibrational state. In this work, NaCl is equilibrated with the flow carrier gas at 300 K, primarily populating only the ground and first excited vibrational states (83% and 14%, respectively), so that narrower peaks are not surprising.

The absolute magnitudes of the integrated cross sections for the data above 220 nm (see following discussion) calculated from the two sets of data pose a greater problem in that they differ by a factor of six. The quoted error bars on both experiments do not account for this discrepancy and one suspects that either or both experiments contain systematic errors. One possible explanation is the presence of NaCl dimers in the high temperature experiments. Davidovits and Brodhead determined their absorption cross sections assuming that NaCl monomer, calculated from tabulated vapor pressure curves, was the sole absorber in their cell. They also estimated the fraction of (NaCl)$_2$ in their experiments to be 40%-60%. If these absorbed light to
form either Na + NaCl₂ or 2NaCl, the overall number density of absorbers would be larger and the reported cross section values lower.

No dimers are present in our experiments. Sodium chloride is formed by chemical reaction in a flowing carrier gas and there are insufficient collisions for dimerization to occur via termolecular recombination. Lamb and Benson⁵⁸ have calculated the rate constant for

\[ 2\text{NaCl} + M \rightarrow (\text{NaCl})_2 + M \]  

(10)

to be \( k = 10^{-28.5} \text{ cm}^6 \text{ molecule}^{-2} \) at 230 K. Assuming this value to be approximately the same at 300 K, less than .002 of the nascent NaCl dimerizes over the path between where it is formed and the photolysis volume.

Absorption in the ultraviolet has been observed for dimeric species such as (NO)₂ and (N₂O)₂.²⁶⁻²⁸ These absorptions occur in the same spectral region as absorptions of the monomer and, at least in the case for (NO)₂, exhibits a large oscillator strength.²⁶ This suggests that it is possible for even a weakly bound dimer to exhibit a strong UV absorption cross section. On the other hand, Su and Riley did not observe any anomalous features in their time-of-flight recoil distributions of alkali halides, photodissociated at 266 nm, which suggest the presence of dimers.⁷⁻⁹ Oppenheimer and Berry did not observe any features attributable to dimers for matrix isolation measurements of LiI, NaBr, and NaI, where dimers would be expected to be present.²⁹ For NaCl, KI, RbBr, and LiBr, no absorption bands attributable to any species were observed.
The only other comparable alkali halide cross section measurement at room temperature is that for CsI by Grossman et al. The results are consistent with our measurements for NaCl. The spectral width for this $1^{-1}L^+$ transition (in Hund's case c notation) is narrower and the integrated cross section is a factor of two smaller than that reported by Davidovits and Brodhead. Furthermore, cesium iodide dimers are not expected to be present in either experiment.

**Cross Section Calculations**

The ionic ground electronic state for the lighter alkali halides is designated $X^1E^+$ (Hund's case a), and correlates to separated $M^+ + X^-$ ions. Excited molecular states correlating with neutral atoms $M + X$ are covariant, and for $\text{Na}(^{2}S) + \text{Cl}(^{2}P_j)$, are represented by Hund’s case c angular momentum coupling as $\Omega = 0^+, 0^-, 1$, and $2$. Only $0^+ \leftrightarrow 1^+$ (parallel) and $1^+ \leftrightarrow 2^+$ (perpendicular) transitions are allowed. The potential curve for the ground electronic state of these molecules is fairly well represented by a modified Rittner potential, reproducing experimentally measured dissociation energies and anharmonic constants with reasonable accuracy (see Figure 3).

The first few electronic excited state potentials are not well characterized. They are thought to be either repulsive or only slightly bound. Zefri and Balint-Kurti have calculated the ground and first four excited electronic state potentials and associated transition dipole moments for a group of alkali halides using a semi-empirical valence-bond method, while excluding the effects of spin-orbit coupling. Within the framework of this Hund’s case a approach, they find that the excited states
are all fairly repulsive (see Figure 3) and that use of the Franck-Condon approximation is invalid here as the transition dipole moments vary considerably with internuclear separation, r. Their excited state curves are labelled in $^1\Sigma^+$ (parallel) and $^1\Pi$ (perpendicular) notation.

In order to gain a clearer understanding of our results, we have calculated NaCl absorption cross section curves over the wavelength range 180-300 nm for comparison with our experimental data. We use the reflection approximation\(^{32}\) in which the electronic transition moment is calculated using a harmonic oscillator wavefunction for the ground electronic state, a $\delta$-function for the upper repulsive state wavefunction, and Zeiri's transition dipole moments at each value of r. At 300 K, only $v=0$ and $v=1$ are sampled, so that the harmonic oscillator potential accurately represents the Rittner form (see insert in Figure 3). Small corrections for the displacement of higher vibrational levels from the equilibrium internuclear separation $r_e$, and for the effect of thermally-averaged rotational populations on the absorption wavelengths were also included in this calculation.

Figure 4 compares the calculated and experimental data. In all cases, the total integrated cross section for the sum of the A-X and B-X transitions for calculated curves have been normalized to that of the experimental curves. The dotted curve in Figure 4a shows absorption curve at 300 K calculated from the potentials of Zieri and Balint-Kurti.\(^1\) This curve, which does not match the experimental data (represented by the solid curve), is shifted to much shorter wavelengths and exhibits one broad peak. Transitions to both the $^1\Pi$ and $^1\Sigma^+$ states lie under this peak. Excitations to higher states lie further into the ultraviolet.
To better reproduce our experimental results, we varied the energies and shapes of the A$^1\Pi$, B$^1\Sigma^+$, C$^1\Pi$, and D$^1\Sigma$ states in a narrow region of ±0.25 Å about r_e = 2.36 Å. This range corresponds to the values of ρ over which the square of the lowest five vibrational wavefunctions are important. For v = 0 and v = 1, only the region ±.10 Å about r_e contributes to σ, and the best fit to our data only senses this range of r. The results of this fit to our data are shown as the dashed curve in Figure 4a and results from lowering all four curves and flattening the A and B states in the region about r_e (Figure 3). These new curves are reasonable in light of the approximations made by Zeiri and Balint-Kurti. They state that no valence-bond structures corresponding to Rydberg states were included in their calculations, and the inclusion of these states would have made their calculated repulsive curves less repulsive.

The peaks at 235 nm and 260 nm in Figure 4a represent the B-X (parallel) and A-X (perpendicular) transitions, respectively. At wavelengths shorter than 220 nm, the C-X (and D-X) transition causes the cross section to rise, as observed in the data. We do not observe the peak absorption for this transition, so the shape and position of the C$^1\Pi$ data is less well determined than the A or B states. Nevertheless, the fact that this rise is seen at all near 200 nm strongly suggests that the C$^1\Pi$ state is bound, lying at energies which are equal to or slightly lower than the energy of its dissociation products, Na($^2P$) + Cl($^2P_f$). This has been observed for this state in other alkali halides.
The relative heights of the calculated peaks at room temperature agree qualitatively with the experimental data (normalized to total integrated cross section), suggesting that Zeiri's transition dipole moment calculations are approximately correct. Su and Riley measured the ratio of the parallel to total transition moments at 266 nm for a series of alkali halides using a molecular beam recoil velocity technique. They find that the amount of parallel character drops from about 60% for the iodides to less than 30% for alkali chlorides. This ratio for NaCl was determined to be 0.16±0.02. At the temperature of their source (1189 K), we calculate a ratio of 0.28.

Using the potentials which were fit to our room temperature data, we computed the absorption spectrum at 1123 K for comparison with the experiments of Davidovits and Brodhead. Despite the limitations of the calculation (and uncertainties in extending them to high temperatures), we see in Figure 4b that the agreement is remarkably good. The higher degree of structure in our calculations than were observed by Davidovits can be explained as arising from regions of r outside of r±.10 Å, so that small changes in the shapes of the potentials there would shift the absorption wavelengths and peak shapes for the excited vibrational states. Slightly steeper curves for r<2.2 Å would tend to broaden the absorption peaks for the higher vibrational states and lead to a smoother overall absorption curve.

In comparing the calculated ratio of the parallel to perpendicular transition probabilities to those observed by Davidovits and Brodhead, Su and Riley, and ourselves, this ratio is systematically high. This suggests that
the B-X dipole transition moments of Zieri and Balint-Kurti\textsuperscript{14} are too large relative to those of the A-X transition.

In conclusion, photodissociation cross section measurements of NaCl at 300 K have resolved the A-X and B-X electronic transitions. From these spectra, more accurate potential curves for the \( A^1\Pi \) and \( B^1\Sigma^+ \) electronic states have been derived in the region about the equilibrium internuclear distance of the NaCl ground state. The shape of the photodissociation spectrum is consistent with the photoabsorption spectrum of Davidovits and Brodhead,\textsuperscript{4} measured at 1123 K. However, the absolute magnitude of the integrated cross section in this work is about six times smaller than that of Davidovits. The most likely explanation is that the presence of dimers in the high temperature studies contributed to the observed absorption.

**Stratospheric Photolysis of NaCl**

The photolysis of NaCl is crucial in determining the extent to which alkali metals of meteoric origin affect the ozone balance in the upper stratosphere.\textsuperscript{15-17} Convoluting the measured total solar flux at 40 km (including albedo and scattering)\textsuperscript{33} over our measured cross sections between 180 and 300 nm, we obtain a total photolysis rate \( J \) of \( 1.9 \pm 0.8 \times 10^{-6} \text{ s}^{-1} \). Based on our calculations for cross sections, the curve at stratospheric temperatures (-260 K) is nearly the same as our 300 K results. This number is a factor of ten smaller than that estimated by Rowland and Rogers\textsuperscript{17} using the high temperature data of Davidovits and Brodhead.\textsuperscript{4} The difference is due to two factors. First, the solar flux has a local minimum near 250 nm and falls off rapidly below 200 nm, offsetting much of the contributions of our
peaks near 190, and 235 nm (Figure 5). Second, the rapid rise in the solar flux above 270 nm overemphasizes excited vibrational state contributions to the cross section, which are absent at 40 km altitude (260 K).

Using \( J = 1.9 \times 10^{-6} \text{ s}^{-1} \) and the measured rate constants for reactions 1 - 3, the rate at which free chlorine is released from HCl at 40 km is \(-10^{-6} \text{ s}^{-1}\), where the photolysis of NaCl is the rate limiting step. This calculation assumes a total gas phase alkali concentration of \( 5 \times 10^5 \text{ cm}^{-3} \). For comparison, the release rate of Cl for HCl by OH (i.e. \( k_5 \cdot [\text{OH}] \)) is \( 6.7 \times 10^{-6} \text{ s}^{-1} \), based on an OH concentration of \( 10^7 \text{ cm}^{-3} \) and the value \( k_5 (260 \text{ K}) = 6.7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \). Thus we conclude that, depending on the altitude at which heterogeneous and homogenous removal processes of atmospheric alkali compounds dominate gas phase chemistry, meteoric alkali chemistry could be an additional and important source of free chlorine in the upper stratosphere. We are presently investigating the magnitudes of processes through which atmospheric alkali compounds might be removed from the gas phase.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge helpful discussions with the late Professor Frederick Kaufman and the technical assistance of Warren E. Goodwin. This work was sponsored by the Fluorocarbon Program Panel of the Chemical Manufacturers Association under Contract No. FC-84-494 and by the Air Force Geophysics Laboratory under Contract No. F19628-83-C-0010.
REFERENCES


FIGURE CAPTIONS

1. Schematic of the experimental apparatus for photodissociation of NaCl. Components are identified as follows: M = mirror; A1, A2, and A3 = apertures; F1 = BK-7 window acting as a UV absorbing filter; F2 = 590 nm interference filter; L1 and L2 = lenses; B = Quartz slide acting as a beamsplitter; D = fast UV photodiode detector.

2. Plot of experimental data versus wavelength of photodissociation cross sections for NaCl at 300 K. Error bars represent one standard deviation. A dashed curve is drawn through the points to highlight the shape of the data.

3. Potential curves used in the calculation of NaCl photodissociation cross sections. Dashed lines are the calculated curves of Zeiri and Balint-Kurti. Solid lines (for A^1Π, B^1Σ^+ and C^1Π) are derived as discussed in the text. The insert shows the lowest part of the X^1Σ^+ potential, and illustrates how the harmonic oscillator approximation (solid curve) compares with the Rittner potential (dashed curve) for the lower vibrational levels.

4. Plots of experimental data versus calculated cross section curves. a) 300 K data using representative experimental curve from Figure 1. b) 1123 K data of Davidovits and Brodhead. The computed curves have been normalized to have equal total integrated cross sections above 220 nm (sum of the A-X and B-X transitions).

5. Plot of the calculated photolysis rate of NaCl as a function of wavelength at 40 km altitude.
OPTICAL LAYOUT FOR MEASUREMENT OF PHOTODISSOCIATION CROSS SECTIONS

Excimer Laser

Raman Shifter

N₂ Laser  →  Dye Laser  →  Optical Fiber

He, Cl₂

Flow Tube

Na Oven

Power Meter

Pump

M

A1

A2

A3

F1

L1

B

F2

L2

PMT Fluorescence Monitor
This Work — Calculated (best fit)

Calculated (from ref. 14)

Davidovits and Brodhead (ref. 4)

Calculated

T = 300K

WAVELENGTH (nm)

T = 1123K
7. RATE CONSTANT FOR THE REACTION OF NaOH WITH CO₂

7.1 Introduction

In addition to the chemical oxidation reactions of sodium involving oxyhydrogenic species, Murad et al.¹ suggested that reactions with CO₂ might also be important in both the mesosphere and upper stratosphere. At higher altitudes, the reaction

\[
\text{NaOH} + \text{CO}_2 + \text{M} \rightarrow \text{NaHCO}_3 + \text{M}
\] (1)

may serve as an additional sink for sodium. With CO₂ abundances of >10⁸ cm⁻³ at 100 km and increasing at lower altitudes, this reaction could control the fate of Na even if \(k_1\) were small. Near 40 km, the reaction

\[
\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{CO}_3
\] (2)

might augment or supplant the NaO, NaO₂, and NaOH reactions with HCl as sources for NaCl is the catalytic Cl release mechanism.

The goal of this task was to measure a room temperature rate constant for reaction 1 at a pressure of a few torr to estimate the importance of CO₂ in the chemistry of atmospheric sodium. Detection of NaOH in these experiments was to be accomplished using infrared diode laser absorption of the \(ν_1\) transition (Na-OH stretch vibrational mode). Within the constraints of time and resources allocated for this task, we were unable to locate the \(ν_1\) mode and were therefore unable to perform the rate measurements. A brief description of the steps taken in performing these measurements follows.
7.2 Formation of Gas Phase Sodium Hydroxide

Gas phase sodium hydroxide is produced at room temperature in a conventional flow tube by two different reaction sequences. The direct method involves the addition of hydrogen peroxide to atomic sodium,

\[
\text{Na} + \text{H}_2\text{O}_2 \rightarrow \text{NaOH} + \text{OH} + \text{NaO} + \text{H}_2\text{O}
\]

(3a)

(3b)

This reaction has been studied previously\(^2\) and it has been shown that 
\[k_{3a}/k_{3a} + k_{3b} = 0.6.\] This ratio can be raised to unity upon the addition of excess CO, which reacts only with sodium monoxide and creates a chain reaction sequence resulting in the eventual conversion of all of the sodium to NaOH:

\[
\text{NaO} + \text{CO} \rightarrow \text{Na} + \text{CO}_2
\]

(4)

The second NaOH production method is a two-step conversion of atomic sodium using N\(_2\)O and H\(_2\):

\[
\text{Na} + \text{N}_2\text{O} \rightarrow \text{NaO} + \text{N}_2
\]

(5)

\[
\text{NaO} + \text{H}_2 \rightarrow \text{NaOH} + \text{H} + \text{Na} + \text{H}_2\text{O}
\]

(6a)

(6b)

In excess N\(_2\)O and H\(_2\), reactions 5 and 6 cycle until NaOH is the sole product. The value of \(k_5 = 8 \times 10^{-13} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}\) was measured by us and is discussed in Section 3 of this report. Ager and Howard report the
\[ k_{5a} = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and } k_{5b} = 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \]

In all cases atomic sodium concentrations were monitored using laser induced fluorescence. Although this method does not produce a signal linear to the sodium concentration at values of \([\text{Na}] > 10^{11} \text{ cm}^{-3}\), it can be used to show when all of the Na has been chemically removed (our sensitivity to sodium in these experiments is estimated at \(10^7 \text{ cm}^{-3}\)). Absolute determination of the sodium concentration in our detection zone was accomplished by titration with known amounts of Cl\(_2\). In these experiments, \([\text{Na}]\) was varied from \(-10^{12} - 3 \times 10^{14}\) atoms \text{ cm}^3. Although we did not detect NaOH directly, we still believe that it was produced in concentrations equivalent to the \([\text{Na}]\) in the system. Besides observing the loss of Na upon addition of H\(_2\)O\(_2\) or N\(_2\)O, we also could observe, for the first NaOH production method, changes in infrared H\(_2\)O\(_2\) absorptions which approximately correspond to the magnitude of the Na concentration changes. Furthermore, past experience has shown that upon addition of H\(_2\)O\(_2\) to Na, OH appears\(^2\) (seen via laser induced fluorescence), presumably as the product of reaction 3a.

7.3 Detection of NaOH

The methods and techniques for measuring infrared absorption of gaseous species with tunable diode lasers has been well described elsewhere.\(^6-5\) This method was chosen for the detection of NaOH since it is expected to be fairly sensitive, given the expected large dipole moments of alkali compounds.\(^6-8\) No viable visible or ultraviolet optical detection techniques have been demonstrated.

The infrared absorption spectrum of NaOH is not well known. Sodium hydroxide is a linear molecule,\(^9-10\) and has three infrared active vibrational modes - a low frequency bend, an Na-OH stretch, and an O-H stretch. Observation of the latter two modes of NaOH or polymeric forms of NaOH have been reported. Spinar and Margrave\(^11\) heated powdered NaOH in an absorption cell to 850 - 1000 degrees (Celsius?) and using a broadband source of light,
observed a feature centered at 437 ± 10 cm\(^{-1}\), which they attributed to [NaOH]\(_x\). Acquista and Abramowitz\(^{10}\) made broadband absorption measurements of NaOH and NaOD on an argon matrix and reported seeing a number of bands between 200 and 600 cm\(^{-1}\). Their source of NaOH was a Knudsen cell with a double boiler arrangement which they felt could help distinguish between monomer and polymer bands by changing the oven temperatures. Large isomer shifts led to the assignment of 337 ± 1 cm\(^{-1}\) as the \(v_2\) mode. Certain changes in intensity of the 431 ± 1 cm\(^{-1}\) band relative to the other bands led them to tentatively assign this feature to the \(v_1\) band of NaOH. However, they observed but did not assign strong absorptions at 400, 360, 285, and 273 cm\(^{-1}\). Although the assignments for \(v_1\) in these two experiments agree fairly well, it must be noted that the frequencies obtained in matrix isolation studies are lower than the corresponding frequencies found in the gas phase.\(^{12}\) In fact, alkali metal compounds may exhibit the largest differences. The alkali halides show gas phase frequencies which are 6-9% higher than the corresponding argon matrix value. If one models the OH ligand as a fluorine atom, then we might expect a frequency shift similar to that of NaF, i.e. 7\%, or an expected value of ~460 cm\(^{-1}\) based on the assignment of Acquista and Abramowitz.\(^{10}\)

Another approach for estimating the location of \(v_1\) is to compare the gas phase \(v_1\) frequencies of other alkali hydroxides and fluorides. For Rb, the difference is 7 cm\(^{-1}\) and for K, 15 cm\(^{-1}\).\(^{11-13}\) For NaF \(v_1 = 529.2\) cm\(^{-1}\),\(^{13}\) so that one might expect a band center in the 480 - 500 cm\(^{-1}\) region.

Finally, theoretical calculations for NaOH have been performed by Long, et al.,\(^9\) using a 6-21G basis with MP3 and CID electronic correlation. The frequencies determined were \(v_3 = 3628\) cm\(^{-1}\) in agreement with predictions of Kuijpers et al.,\(^{14}\) \(v_2 = 322\) cm\(^{-1}\) in good agreement with Acquista and Abramowitz\(^{10}\) (although one might have expected a gas phase prediction somewhat higher than the matrix measurement), and \(v_1 = 710\) cm\(^{-1}\). This last prediction appears high. However, it is unclear from the experiments\(^{10-11}\) whether or not any unassigned absorptions were seen in this spectral region.
7.4 Results

Using second-derivative techniques, infrared absorption spectra were taken at 376, 378, 407.5, 424, 448, 477 and 497 cm\(^{-1}\). Each scan covered a range of at least twice that of the NaOH rotational constant, in order to assure the observation of a rotational line. All measurements were performed using the same diode laser, and detection of the laser beam was made using a liquid nitrogen-cooled Hg: Cd: Te detector which was selected for peak response near 25 \(\mu\)m. A typical spectrum is shown in Figure 7.1. In most of the data, etalons within the White cell limited the measurable fractional absorption limit to about 1%. At the lowest frequencies, both laser power and detector response drop, so that the detection limit was only a few percent absorption. Even with these poor sensitivities, with estimated concentrations of NaOH greater than \(10^{13}\) cm\(^{-3}\), we would expect fractional absorptions greater than one percent and in most of the cases studied greater than ten percent.

No absorption feature attributable to NaOH was observed at any of the frequencies studied. The diode/detection system was working, as evidenced by observation of \(H_2O_2\) absorptions as well as known absorptions of \(CS_2\), which was added to the flow for wavelength calibration purposes.

In order to assure ourselves that the IR diode absorption system could detect alkali species, we looked for absorption lines of KF, made by reacting K with excess \(F_2\). Its vibrational spectrum (actually the first overtone spectrum) has been measured with a diode laser,\(^{15}\) so that the band center is accurately known. The rotational lines were observed at approximately 407.8, 430, and 431.4 cm\(^{-1}\). Based on the measured concentration of potassium and the observed amount of absorption, we conclude that if rotational lines of NaOH are to be seen with the present system, they will appear using more intense laser modes, due to the problems of large internal etalons and system noise. A more thorough search using a number of diodes (to assure complete wavelength coverage at reasonable intensity) should be able to detect NaOH at levels useable for simple kinetic measurements.
The lack of an observed NaOH absorption feature leads us to the conclusion that the previously detected bands near 430-440 cm$^{-1}$ do not belong to monomeric NaOH or that we happened to look exactly at band center, where the spacing between the P(1) and R(0) lines would exceed the spectral range of the scan at that diode frequency. It is clear that this problem needs further investigation.
Figure 7.1 Typical Second-Derivative Absorption Spectrum for Na+H₂O₂. Upper curve is with both reactants present. Lower curve is with the sodium oven turned off.
References

8. DISCUSSION AND SUMMARY RESULTS

From the work presented in the preceding sections, it is clear that a great deal of progress has been made in the past five years in both recognizing and then understanding the role which sodium compounds of meteoric origin play in atmospheric chemistry. A list of the reactions of sodium compounds rate constants measured during this period is shown in Table 8-1. We now believe that the observed mesospheric atomic sodium profile can be explained, and its diurnal and seasonal variations understood.\(^{12-14}\) A schematic diagram which illustrates the evolution of sodium from the time it enters the lower thermosphere to its removal from the stratosphere is shown in Figure 8.1.

We see that as the ablated sodium metal in its neutral form descends below \(-100\) km, it begins to react with ozone and molecular oxygen. The latter reaction dominates below 85 km as the O\(_2\) concentration and total atmospheric pressure increase. Sodium monoxide reacts at these altitudes with atomic oxygen to produce electronically excited sodium atoms, which emit the familiar D-line radiation at 590 and 596 nm.

As atomic sodium disappears below 80 km, it is converted through the above mechanisms to NaO and NaO\(_2\). The NaO rapidly reacts with any traces of water vapor to produce NaOH. At these altitudes, photolysis will recycle these species to atomic sodium, resulting in a steady state mixture of mostly NaO\(_2\) and NaOH, with little NaO and virtually no atomic sodium. The question of which of the first two compounds dominates will depend on how rapidly NaO\(_2\) is converted to NaO (see Figure 8.1) relative to its photodissociation rate. These reaction rate constants and photolysis rates have not yet been measured.

Once the alkali end products of the mesospheric chemistry reach the upper stratosphere, reactions with chlorinated compounds, most notably HCl, become important. Photolysis of NaCl will cause atomic chlorine to be released,
# Table 8-1 Recent Experimental Rate Constants of Gas-Phase Sodium Compounds

<table>
<thead>
<tr>
<th>Reaction</th>
<th>T(K)</th>
<th>$k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Na} + \text{O}_2 + \text{M} + \text{NaO}_2 + \text{M}$ [(\text{M} = \text{N}_2)]</td>
<td>320-698</td>
<td>$(1.9 \pm 0.4) \times 10^{-30} (T/300)^{-1.1 \pm 0.5}$</td>
<td>Silver, et al.$^1$</td>
</tr>
<tr>
<td></td>
<td>571-1016</td>
<td>$(1.11 \pm 0.08) \times 10^{-23} T^{2.4 \pm 0.14}$</td>
<td>Husain, et al.$^2$</td>
</tr>
<tr>
<td></td>
<td>1650-2400</td>
<td>$2 \times 10^{-28} T^{-1}$</td>
<td>Hynes, et al.$^3$</td>
</tr>
<tr>
<td>$\text{Na} + \text{O}_3 + \text{NaO} + \text{O}_2$</td>
<td>293</td>
<td>$(3.01 \pm 0.4) \times 10^{-10}$</td>
<td>Silver, Kolb$^6$</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>$(7 \pm 2) \times 10^{-10}$</td>
<td>Ager, Howard$^5$</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>$4(\pm 4, -2) \times 10^{-10}$</td>
<td>Husain, et al.$^6$</td>
</tr>
<tr>
<td>$\text{Na} + \text{N}_2\text{O} + \text{NaO} + \text{N}_2$</td>
<td>295</td>
<td>$(7.7 \pm 0.9) \times 10^{-13}$</td>
<td>Silver, Kolb$^6$</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>$(8.2 \pm 1.5) \times 10^{-13}$</td>
<td>Ager, Howard$^5$</td>
</tr>
<tr>
<td></td>
<td>349-917</td>
<td>$(1.9 \pm 0.3) \times 10^{-10}$</td>
<td>Husain, Marshall$^7$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\exp (-12.5 \pm 0.6 \text{ kJ/mole/RT})$</td>
<td></td>
</tr>
<tr>
<td>$\text{Na} + \text{Cl}_2 + \text{NaCl} + \text{Cl}$</td>
<td>294</td>
<td>$(6.7 \pm 0.9) \times 10^{-10}$</td>
<td>Silver$^8$</td>
</tr>
<tr>
<td></td>
<td>284-305</td>
<td>$(1.08 \pm 0.2) \times 10^{-9}$</td>
<td>Talcott, et al.$^9$</td>
</tr>
<tr>
<td>$\text{Na} + \text{H}_2\text{O}_2 + \text{NaOH} + \text{OH}$ [+ \text{NaO} + \text{H}_2\text{O}]</td>
<td>308</td>
<td>$4.1 \times 10^{-11}$</td>
<td>Silver, et al.$^{10}$</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>$2.8 \times 10^{-11}$</td>
<td>Silver, et al.$^{10}$</td>
</tr>
<tr>
<td>$\text{NaO} + \text{O}_3 + \text{NaO}_2 + \text{O}_2$</td>
<td>293</td>
<td>$1.5 \times 10^{-10}$</td>
<td>Silver, Kolb$^4$</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>$1.8 \times 10^{-10}$</td>
<td>Ager, Howard$^5$</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>$5 \times 10^{-11}$</td>
<td>Silver, Kolb$^4$</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>$1 \times 10^{-10}$</td>
<td>Ager, Howard$^5$</td>
</tr>
<tr>
<td>$\text{NaO} + \text{H}_2\text{O} + \text{NaOH} + \text{OH}$</td>
<td>290</td>
<td>$(2 \pm 1) \times 10^{-10}$</td>
<td>Ager, Howard$^5$</td>
</tr>
<tr>
<td>$\text{NaO} + \text{HCl} + \text{NaCl} + \text{OH}$</td>
<td>308</td>
<td>$2.8 \times 10^{-10}$</td>
<td>Silver, et al.$^{10}$</td>
</tr>
<tr>
<td>$\text{NaO} + \text{H} + \text{Na} + \text{OH}$</td>
<td>308</td>
<td>$&gt;4 \times 10^{-12}$</td>
<td>Silver, et al.$^{10}$</td>
</tr>
<tr>
<td>$\text{NaO}_2 + \text{HCl} + \text{NaCl} + \text{HO}_2$</td>
<td>295</td>
<td>$(2.3 \pm 0.4) \times 10^{-10}$</td>
<td>Silver, Kolb$^7$</td>
</tr>
<tr>
<td>$\text{NaOH} + \text{HCl} + \text{NaCl} + \text{H}_2\text{O}$</td>
<td>295</td>
<td>$(2.8 \pm 0.9) \times 10^{-10}$</td>
<td>Silver, et al.$^{10}$</td>
</tr>
<tr>
<td>$\text{NaOH} + \text{H} + \text{Na} + \text{H}_2\text{O}$</td>
<td>295</td>
<td>$&gt;4 \times 10^{-12}$</td>
<td>Silver, et al.$^{10}$</td>
</tr>
<tr>
<td>$\text{NaCl} + \text{H} + \text{Na} + \text{HCl}$</td>
<td>308</td>
<td>$5 \times 10^{-14} \pm 1$</td>
<td>Silver, et al.$^{10}$</td>
</tr>
<tr>
<td>$\text{NaCl} + \text{hv} + \text{Na} + \text{Cl}$</td>
<td>300</td>
<td>$\sigma_{\text{max}} = 1 \times 10^{-17} \text{ cm}^{-2}$ at 235 nm</td>
<td>Silver, et al.$^{11}$</td>
</tr>
</tbody>
</table>

(a) rate constant in units of cm$^6$ molecule$^{-2}$ s$^{-1}$

8-2
Figure 8.1 Schematic Diagram of Meteoric Sodium Chemistry
creating an additional source for chlorine catalyzed destruction of stratospheric ozone.

The importance of sodium catalyzed chlorine release relative to that caused by the reaction of OH with HCl remains to be determined. If only these gas phase processes are considered, this process might well increase the previously recognized chlorine release rate by as much as 30 percent. However, one must consider both homogeneous and heterogeneous loss processes for these atmospheric metal species. The most likely pathways for losses are condensation onto atmospheric dust, smoke, water droplets or other aerosols. No experimental data quantifying the magnitude of these effects exist, and simple estimates of the effectiveness of alkali loss range from no removal to total removal, depending on one's choice of parameters. Because of the potential importance on stratospheric ozone, we believe that in situ measurements of the stratospheric gas phase alkali content are required.

Finally, we would like to point out that sodium comprises only a few percent of meteoric metals, and that the effects of the more abundant species on atmospheric chemistry should be investigated. This is especially true for iron and silicon. The former is expected to exhibit a fair bit of reactivity with atmospheric constituents. Although silicon oxides are fairly stable, their reactions with halogen compounds are only beginning to be understood and this area should be studied more thoroughly.

8.1 References


9. PAPERS AND PRESENTATIONS

This section lists the papers published and presentations made of the reactions studied in this program.

9.1 Publications


9.2 Presentations


