above.

the fluorine atom densities employed in these experiments are such that the time constant of the $F + HN_3$ reaction is very short (mixing limited), the N_3 density can be described as an exponential decay

$$[\mathbf{N}_3] = [\mathbf{N}_3]_0 e^{-(k_w + k_q[\mathbf{Q}])t}$$
(5)

where $[N_3]_0$ is the "initial" N_3 density produced by F + HN₃ (approximately equal to the initial HN₃ density), k_w is the measured wall removal rate (46 s⁻¹), and $k_q[Q]$ refers to the rate of pseudo-first-order removal by other species Q (e.g., excess fluorine atoms, HF, or added N atoms). We propose the following model to describe the time dependence of the nitrogen atom density:

$$N_3 \xrightarrow{k_w} N + N_2 \tag{6}$$

$$N \xrightarrow{k_3[N_3]} N_2 + N_2 \tag{3}$$

$$\mathbf{N} \xrightarrow{k^{N}_{w}} {}^{1}/{}_{2}\mathbf{N}_{2} \tag{7}$$

In reaction 3, N atoms are removed at a pseudo-first-order rate $k_3[N_3]$. Although the N₃ density decays in time as in eq 5, this decay (on the order of 100 s⁻¹) is slow relative to the time constant of reaction 3 (on the order of 1000 s⁻¹ for a typical HN₃ flow rate). Reaction 7 describes first-order removal of N atoms by the reactor walls at a rate k^{N}_{w} . Although this process is in principle much slower than reaction 3, it may affect the N₂ first positive intensity when the N₃ density is low. From reactions 5, 6, 3, and 7, the time dependence of the N atom density is given by a sum of rising and falling exponential terms

$$[\mathbf{N}] = C_1 e^{-(k_w + k_q[\mathbf{Q}])t} - C_2 e^{-(k_3[\mathbf{N}_3] + k^{\mathbf{N}_w})t}$$
(8)

where C_1 and C_2 are constants. Note that the exponential in $[k_3[N_3] + k^{N_w}]$ reflects the apparent rise of the N atom density. The intensity of the N₂ B \rightarrow A emission is proportional to [N] [N₃]:

 $I \propto C_1' e^{-2(k_w + k_q[Q])t} -$

$$C_{2}' \exp(-(k_{3}[N_{3}] + k_{w}^{N} + k_{w} + k_{q}[Q])t)$$
 (9)

In the experiments with the Pyrex inserts in the Teflon reactor, the decay of the N_2 emission was found to be unchanged relative to the decay without the inserts (suggesting that k_w and $k_q[Q]$ are unchanged), but the overall intensity was reduced. From the model presented above, we interpret this observation to reflect an enhanced removal of N atoms by the Pyrex surface (i.e., a larger k^{N}_{w}). In reality, the surface was not "clean" Pyrex but Pyrex exposed to a substantial flow of fluorine atoms and HF. This model also offers an explanation for the widely varying values of the apparent $N_3 + N_3$ rate constant reported by several authors.^{2,3} When the experimental circumstances are such that only a small proportion of the azide radicals dissociate (as in the present case), the $N + N_3$ reaction has a minimal effect on the overall rate of N_3 removal and this rate is determined to be slow. For conditions which favor greater fractional dissociation of N₃, the chain driven by $N + N_3$ may result in a very large apparent N_3 removal rate. Indeed, production of N₃ under conditions where a large fraction (50%) dissociates may well offer a rapid and efficient source of $N_2(B)$ and $N_2(A)$ metastables, species which have been considered as energy storage agents for potential laser systems.

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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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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. A room temperature rate constant of this reaction is found to be $(3.1 \pm 0.4) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. The rate constant for the NaO + O₃ reaction is determined to be about 2×10^{-10} cm³ molecule⁻¹ s⁻¹, with 0.7 ± 0.2 of the products being NaO₂ + O₂ and the remainder Na + 2O₂. Also measured is the rate constant for Na + N₂O \rightarrow NaO + N₂, found to be $(7.7 \pm 0.9) \times 10^{-13}$ cm³ 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.

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

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the major sink for atomic sodium above 85 km, and knowledge of its rate constant is critical for modeling the 70–95-km NO layer

and in understanding the processes leading to the sodium D line

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

prior to 1982 almost no kinetic data existed for most of the reactions used in these models. The earlier models utilized rate constants that were estimated from analogy with atomic hydrogen reactions. In 1976, Kolb and Elgin¹⁶ 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 past few years that direct measurements of alkali rate constants have been made to confirm these suggestions.^{18–25}

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

$$Na + O_3 \rightarrow NaO + O_2$$
 $\Delta H^{o}_r = -167 \pm 42 \text{ kJ mol}^{-1} (1)$

 $Na + N_2O \rightarrow NaO + N_2$ $\Delta H^{o}_{r} = -106 \pm 42 \text{ kJ mol}^{-1}$ (2)

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We also present information on the approximate rate constant and product branching ratio for the reaction of sodium monoxide with ozone.

$$NaO + O_3 \rightarrow NaO_2 + O_2$$
 (3a)

$$Na + 2O_2$$
 (3b)

These and other recent results will help to provide a clearer picture of the chemistry of meteor metals in the mesosphere.

Experimental Section

Rate-constant determinations are made in a fast-flow reactor, which is illustrated in Figure 1 and has been described in detail elsewhere.^{18,26} Briefly, the flow reactor is a 7.26-cm-diameter, 120-cm-long alumina tube, with four perpendicular side arms at the tube exit that 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 Monel 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 commerical 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 by using Beer's law and the absorption cross section of 1.15×10^{-17} cm^{2,27} 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-m-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 O_3 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/XT computer for online collection and analysis.

All rate measurement are performed with O₃ or N₂O \gg Na, ensuring pseudo-first-order kinetic conditions. Reaction times were varied from approximately 3 to 40 ms for the ozone reaction and from 1 to 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.^{19,28}

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Figure 2. Pseudo-first-order decays for the Na + O₃ reaction in the presence of hydrogen chloride. $[O_3] = 5.04 (O), 5.34 (O), 8.64 (O), 17.2 (O), 21.8 (A), 36.3 (O); units of 10¹¹ cm⁻³.$



Figure 3. Dependence of corrected pseudo-first-order rate constant on O_1 concentration at 293 K.

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.

$$Na + O_3 \rightarrow NaO + O_2 \tag{1}$$

However, the NaO subsequently reacts with ozone either to produce NaO_2 or to reform atomic sodium.

$$NaO + O_3 \rightarrow NaO_2 + O_2$$
 $\Delta H^{\circ}_r = -282 \pm 47 \text{ kJ mol}^{-1}$
(3a)

$$\rightarrow$$
 Na + 2O₂ $\Delta H^{\circ}_{r} = -119 \pm 42 \text{ kJ mol}^{-1}$ (3b)

If the branching to (3b) is significant, the observed decays of sodium would not be linear (on a semilog plot of signal vs. 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 O_3 by a factor of 100. The reaction of NaO with HCl produces nonreactive NaCl¹⁸

$$NaO + HCl \rightarrow NaCl + OH$$
 (4)

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 $(4.04-36.3) \times 10^{12}$ 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 4 orders of magnitude of sodium concentration. The first-order





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Figure 4. Plot of computed curves for observed Na decay as a function of $[O_3]t$ for a variety of values of k_{3a}/k_3 . This calculation uses $k_1 = 3.1 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ and $k_2 = 2 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. $k_{3a}/k_3 = (a) 0$, (b) 0.5, (c) 0.7, (d) 0.9; (e) $k_{3b} = 0$.

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 vs. 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 $(3.1 \pm 0.4) \times 10^{-10}$ cm³ 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 Husain et al.,²¹ who measured this rate constant to be 4 (+4, -2) × 10⁻¹⁰ cm³ 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 results can be considered only qualitatively correct. Our results are a factor of 2 smaller than that measured by Ager and Howard,²⁵ 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 decays²⁹

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

where a, b, c, 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 2×10^{-10} cm³ molecule⁻¹ 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 [O₃]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

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Figure 5. Pseudo-first-order decays for the Na + N₂O reaction. [N₂O] = 3.97 (O), 10.8 (\oplus), 24.0 (\square), 35.5 (\blacksquare), 48.7 (\triangle), 61.2 (\blacktriangle), 95.4 (\diamondsuit); units of 10¹³ cm⁻³.



Figure 6. Dependence of corrected pseudo-first-order rate constant on N_2O concentrations at 295 K.

that k_3 is approximately 2×10^{-10} cm³ molecule⁻¹ 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 that with ozone. Furthermore, nonlinearities in the semilog plots of signal vs. reaction time are not observed, demonstrating that the reaction of NaO with N2O 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 $(3.97-95.4) \times$ 10^{13} 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 vs. $[N_2O]$ in Figure 6. The resultant rate constant for this reaction is k_2 = $(7.7 \pm 0.9) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 295 \text{ K}$. This is in excellent agreement with an extrapolation to room temperature of results of Husain and Marshall.²⁴ Their value of $k_2 = (1.9 \pm$ $(0.3) \times 10^{-10} \exp(-12.5 \pm 0.6 \text{ kJ/mol/RT}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ was}$ measured over the temperature range of 349-917 K. This also agrees with a room temperature result of $(8.2 \pm 1.5) \times 10^{-13} \text{ cm}^3$ molecule⁻¹ s⁻¹ of Ager and Howard.²⁵

Discussion

The results of this work confirm that the Na + O₃ reaction rate constant approaches the gas kinetic limit, agreeing remarkably



Figure 7. Schematic diagram for mesospheric sodium chemistry.

well with 3.3×10^{-10} cm³ molecule⁻¹ s⁻¹ as 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 \rightarrow 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.

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