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# Gas-Phase Reaction Rate of Sodium Superoxide with Hydrochloric Acid

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Metal compounds originating from meteor ablation may provide 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 that describe these processes. A critical step in this mechanism is the reaction of $NaO_2$ with HCl. The rate constant for this reaction has been measured in a fast-flow reactor at 295 K and found 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.

## Introduction

In the past few years, a number of experimental rate-constant measurements have been completed[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.[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

$$HCl + OH \rightarrow Cl + H_2O \qquad (1)$$

The chemistry of alkali metals in the lower thermosphere and upper stratosphere has been discussed elsewhere[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 $NaO_2$, 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.

$$NaO_2 + HCl \rightarrow NaCl + HO_2 \qquad (2)$$

$$NaO + HCl \rightarrow NaCl + OH \qquad (3)$$

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

$$NaCl + h\nu \rightarrow Na + Cl \qquad (5)$$

$$Na + O_2 \xrightarrow{M} NaO_2 \qquad (6)$$

$$NaO_2 + (O, OH, H, etc.)... \rightarrow NaOH, NaO \qquad (7)$$

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 ($10^{-2}$ to $10^{-3}$ s$^{-1}$), so that the potential rate limiting step(s) to this process is (are) the conversion of $NaO_2$ 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 ($k_1[OH] \simeq 10^{-6}$ 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 $NaO_2 + HCl \rightarrow NaCl + HO_2$. The results of this measurement should help confirm whether or not meteor 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.[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 that 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 from solid Na 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

$$Na + O_2 + M \rightarrow NaO_2 + M \qquad (6)$$

where M = He and $k_6(He) = 1.4 \times 10^{-30}$ cm$^6$ s$^{-1}$ at 295 K.[2] Molecular oxygen ($\sim 10^{15}$ 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.

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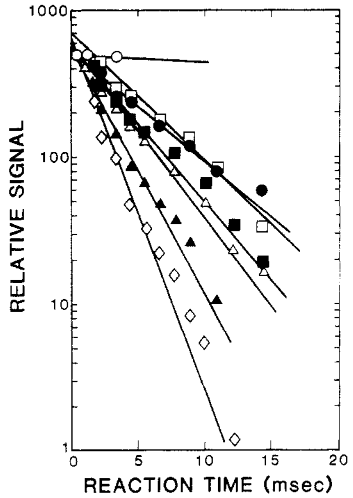

**Figure 1.** Pseudo-first-order decays for $NaO_2$ + HCl reaction. [HCl] = 1.02 (○), 9.21 (●), 12.6 (□), 17.0 (■), 20.9 (△), 35.5 (▲), 41.9 (◇); units of $10^{11}$ molecules $cm^{-3}$.

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.

$$NaO_2 + H \rightarrow Na + HO_2 \quad \Delta H_r = -39 \pm 20 \text{ kJmol}^{-1} \quad (8)$$

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

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 $2 \times 10^{14}$ $cm^{-3}$ 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]

Resonance fluorescence is accomplished by using a 25-W 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 [HCl] ≫ [$NaO_2$], 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.[1,19] The diffusion coefficient for $NaO_2$ in helium was estimated to be 0.3 $cm^2$ $s^{-1}$ at 1 atm, but in fact, the correction for diffusion was quite insensitive to this value (i.e., less than 1% difference if 0.4 $cm^2$ $s^{-1}$ was used).

## Results

Decay of $NaO_2$ for seven concentrations of HCl covering the range 1.02–41.9 × $10^{11}$ $cm^{-3}$ is shown in Figure 1. The first-order decay rates obtained from the slopes of these lines and corrected for diffusion effects are plotted vs. 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 $(2.3 \pm 0.4) \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. The uncertainty expressed in this expression includes precision errors (one standard deviation) as well as estimated errors in accuracy.

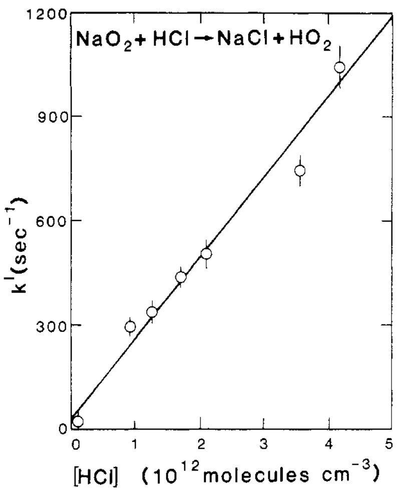

**Figure 2.** Dependence of corrected pseudo-first-order rate constant on HCl concentration at 295 K.

In previous measurements of this type,[1] corrections to the data were required to account for the reaction of NaCl product with the atomic hydrogen titrant

$$NaCl + H \rightarrow Na + HCl \quad (10)$$

We had estimated the rate constant for this reaction as ~5 × $10^{-14\pm1}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. In these experiments, the decays were observed for reaction times varying between 1 and 15 ms, 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 ± 13 kJ $mol^{-1}$ and 134 ± 42 kJ $mol^{-1}$, respectively), the last is most probably barely exothermic by 19 ± 21 kJ $mol^{-1}$. 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 that lead to the formation of an ion-pair adduct, allowing a facile exchange reaction. In this case the adduct would likely be $Na^+(HOOCl)^-$. Although the $(HOOCl)^-$ species has not been observed, it is analogous to the $(HOOH)^-$ ion, which has indirectly been shown to exist although its exact structure is unknown.[23]

Demonstration of a nearly gas kinetic reaction rate constant for $NaO_2$ + HCl supports the possibility that a sodium-catalyzed Cl regeneration mechanism can be fast enough to compete with the OH + HCl reaction in the upper stratosphere. Estimates of total stratospheric sodium concentrations by Liu and Reid[24] are on the order of $5 \times 10^5$ $cm^{-3}$. If most of the sodium is in the form of NaOH, $NaO_2$, or NaO, then the measured rate constants for reactions 2–4 result in a first-order rate constant for HCl reaction of ~1 × $10^{-4}$ $s^{-1}$, much larger than the $10^{-6}$ $s^{-1}$ required for competition with reaction 1. Given the results of this work and a recent study of room temperature NaCl photolysis rates,[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%

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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[26] and ionization/cluster formation,[27] while heterogeneous losses might include condensation onto small particulates[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.

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**Registry No.** $NaO_2$, 12034-12-7; HCl, 7647-01-0.

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# CONDENSED PHASES AND MACROMOLECULES

## Countercurrent Diffusion of $AgNO_3$ and HCl in Cellulose and Nafion Films

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The deposition of silver chloride interlayers in cellulose and Nafion films by countercurrent diffusion of $AgNO_3$ and HCl solutions has been investigated. We have studied the effects of concentration and exposure time on the thickness and position of the interlayer(s). In the case of cellulose, a single, dense interlayer is observed and the process is consistent with a simple reaction-diffusion model. By contrast, with Nafion under certain conditions, multiple interlayers are obtained. These differences are rationalized based on chemical and ion transport properties of the polymers.

### Introduction

Precipitation reactions, including some of the very simplest sort of chemical processes, can give rise to remarkably varied and complex morphological structures, particularly when they are kinetically coupled to physical transport. For example, consider the reaction between two species A and B to yield an insoluble product C, under conditions where either one or both of the reactants are supplied by diffusion across a convection-free reaction medium, such as a gel. Many such systems have been studied. The range of morphological complexity observed for C include examples of large single crystals,[1] dense, sharply defined interlayers (so-called precipitate membranes),[2] and periodic multilayers (Liesegang rings).[3]

A particular experimental arrangement, which we shall refer to as countercurrent diffusion, involves diffusing A and B together from opposite ends of a gel column or sides of a film. This situation has been studied by a number of researchers[4-9] and certain important generalizations have been established. For example, in the cases where a single dense interlayer is deposited (e.g., $BaSO_4$ precipitation in agar[6]), the position of the interlayer has been shown to be purely kinetically controlled. That is, the position corresponds to the point at which the concentrations of $Ba^{2+}$ and $SO_4^{2-}$ are equal to one another and equal to some minimum critical value. Moreover, this concentration is specifically not given by the equilibrium solubility product rule: $K_{sp} = [A][B]$. In fact, the critical concentration may exceed the equilibrium solubility by many orders of magnitude.[5]

Studies of countercurrent precipitation in dense polymer films have been less extensive than in gels. Although the formation of a $BaSO_4$ interlayer in cellulose film was reported almost 30 years ago,[10] the morphology of that interlayer was not characterized. (One such example in cellophane was reported to be only a few microns thick; however, neither the thickness of the film nor the position of the interlayer were given.[6]) A recent report concerning precipitation of insoluble salts in poly(vinyl alcohol) films included an example of complex multilayer formation (similar to Liesegang rings).[11] It appears that the dimensions of precipitated interlayers, to a certain extent, scale with the thickness of the reaction medium. It may, therefore, be appropriate to consider such processes for fabricating new kinds of thin-layer structures.

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