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Gas phase kinetics of the reactions of NaO with H_2, D_2, H_2O, and D_2O

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The gas phase reactions of the NaO radical with H_2, D_2, H_2O, and D_2O were studied in a flow tube reactor at room temperature. The reaction of NaO with H_2 has two exothermic product channels, NaOH + H and Na + H_2O. Both channels were observed and the Na formation channel produces some Na in the $3\ ^2P$ state. The rate constants for the abstraction channel for H_2 and D_2 reactants are $(2.6 \pm 1.0) \times 10^{-11}$ and $(1.1 \times 0.4) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 296 ± 2 K. The reaction of NaO with H_2O was shown to be second order and the products are assumed to be NaOH and OH. The rate constants for H_2O and D_2O reactants are $(2.2 \pm 0.4) \times 10^{-10}$ and $(1.2 \pm 0.2) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} at 298 ± 1 K. The measured NaO + H_2O rate constant is compared to the predicted collision rate constant from a model based on the large attractive dipole–dipole force between NaO and H_2O. The role of these reactions in mesospheric Na chemistry is briefly discussed.

I. INTRODUCTION

The reaction of NaO with water to form NaOH and OH, reaction (1),

$$\mathrm{NaO} + \mathrm{H_2O} \rightarrow \mathrm{NaOH} + \mathrm{OH},$$
$$\Delta H^\circ_{298} = -1.4 \pm 3\ \mathrm{kcal\ mol^{-1}}, \quad (1)$$

was first proposed by Ferguson[1] in 1978 as a step in the reaction scheme for meteoric sodium in the mesosphere. However, the first extensive modeling study of the mesospheric and stratospheric chemistry of Na compounds[2] did not use reaction (1) and instead relied on HO_2 to convert NaO to NaOH via reaction (2):

$$\mathrm{NaO} + \mathrm{HO_2} \rightarrow \mathrm{NaOH} + \mathrm{O_2}. \quad (2)$$

In a later modeling study, Sze *et al.*[3] used two models, one with $k_1 = 1 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} and one with $k_1 = 0$. Addition of reaction (1) to the model made NaOH the dominant Na species below 85 km. Using the estimates of Refs. 2 and 3 for k_2 and k_1, respectively, the first order rate constant for reaction (1) is $\sim 10^5$ times faster than that of reaction (2). Since the product of reaction (1), NaOH, is thought to be an important reservoir species for sodium in the mesosphere and stratosphere, it is clear that the measurement of k_1 is of great importance.

Reaction (1) is not strongly exothermic, $\Delta H^\circ_{298} = -1.4 \pm 3$ kcal mol^{-1}. The uncertainty in the reaction enthalpy is due to uncertainties in the thermochemistry of NaO and, to a lesser extent, NaOH. It is conceivable that this reaction is endothermic and slow. The sole experimental study[4] of the thermochemistry of NaO obtained $\Delta H^\circ_{f,298}$ (NaO) $= 24.3 \pm 4$ kcal mol^{-1}. Theoretical studies[5–7] have predicted values in the range 25–27 kcal mol^{-1}. We have used the value of 24.8 ± 1 kcal mol^{-1} suggested by the recent review of Lamoreaux and Hildenbrand[8] in calculating the reaction enthalpies. For $\Delta H^\circ_{f,298}$ (NaOH) we use -43.8 ± 2.0 kcal mol^{-1} from the combustion flame study of Kelly and Padley.[9]

The reaction of NaO with H_2 has two exothermic product channels:

$$\mathrm{NaO} + \mathrm{H_2} \rightarrow \mathrm{NaOH} + \mathrm{H},$$
$$\Delta H^\circ_{298} = -16.5 \pm 3\ \mathrm{kcal\ mol^{-1}}, \quad (3a)$$
$$\rightarrow \mathrm{Na} + \mathrm{H_2O},$$
$$\Delta H^\circ_{298} = -56.7 \pm 3\ \mathrm{kcal\ mol^{-1}}. \quad (3b)$$

Channel (3b) is sufficiently exothermic to populate the first excited electronic state of Na and produce Na *D* line chemiluminescence.

Reactions (1) and (3) have not been studied previously in the gas phase. We have used deuterium isotope substitution in the H_2O and H_2 reactants to attempt to elucidate the mechanisms of these reactions.

II. EXPERIMENTAL

The NaO source and detection method are identical to those used previously to measure the rate constant for NaO + O_3 and are described elsewhere.[10] Briefly, Na atoms from an oven source are converted to NaO in a 5.1 cm i.d. flow tube in an excess of N_2O by the reaction Na + N_2O → NaO + N_2. NaO is detected by chemical conversion to Na using the fast reaction NaO + NO → Na + NO_2 by NO addition just before the detection region. The Na atoms so produced are detected by resonant fluroescence at 590 nm. The detection limit for NaO is approximately 10^4 molecule cm^{-3}.

The first-order rate constants k_{obs} are measured by monitoring the NaO signal as a function of the distance from the Na source to the detection region. The analysis of Brown[11] was used to compensate for the effects of radial concentration gradients and axial diffusion as done previously for Na kinetics.[12] This analysis yielded rate constants that were within 5% of those obtained fom the simple

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analysis of Huggins and Cahn.[13] Brown's computer program requires the diffusion coefficients of NaO in the carrier gases. $D_{\mathrm{NaO,He}}$ and $D_{\mathrm{NaO,N_2O}}$ were measured previously in our laboratory.[10] $D_{\mathrm{NaO,N_2}}$ was estimated to be 240 $\mathrm{cm^2\ Torr\ s^{-1}}$ at 295 K by assuming $D_{\mathrm{NaO,He}}/D_{\mathrm{NaO,N_2}} = D_{\mathrm{Na,He}}/D_{\mathrm{Na,N_2}}$, where $D_{\mathrm{Na,He}}$ and $D_{\mathrm{Na,N_2}}$ have also been measured in our laboratory.[14] The rate constants are insensitive to the exact values of the diffusion coefficients. For example, in a typical NaO + H_2O data set, a 50% change in D_{NaO} causes a $< 1\%$ change in the rate constant.

The concentration of H_2 in the flow tube was calculated using the flow of pure H_2 measured with a calibrated mass flow meter. For the D_2 experiments the flow of a 10.3% D_2 in He mixture was determined immediately after each experiment by measuring the rate of pressure rise in a calibrated volume. In preliminary experiments, the H_2O source was a bubbler operated at atmospheric pressure and 273 K. We found that drops of water occasionally splashed up out of the cooled region causing instabilities in the flow of water vapor. This lead to a large (50%) uncertainty in the preliminary rate constant. Drawing H_2O or D_2O vapor directly from a slightly cooled flask through a heated double needle valve proved to be a much more stable source. The flow of water vapor was determined before and after each experiment by measuring the rate of pressure change in a calibrated volume, As shown in Sec. III, this produced kinetic data with a much better precision than the bubbler source.

The carrier gases He ($>99.9\%$) and N_2($>99.99\%$) were purified in a molecular sieve trap at 78 and 193 K, respectively. The N_2O ($>99.99\%$), H_2 ($>99.999\%$), and D_2 ($>99.6\%$ at. D), H_2O (distilled), and D_2O ($>99.7\%$ at. D) were used as is. In all cases the rate constants were sufficiently large such that any effects from impurity reactions are completely negligible.

III. RESULTS

Both product channels of reactions (3) and (4) were observed.

$$\mathrm{NaO} + \mathrm{H_2} \rightarrow \mathrm{NaOH} + \mathrm{H}, \quad \Delta H^\circ_{298} = -16.5 \pm 3\ \mathrm{kcal\ mol^{-1}}, \tag{3a}$$

$$\rightarrow \mathrm{Na} + \mathrm{H_2O}, \quad \Delta H^\circ_{298} = -56.7 \pm 3\ \mathrm{kcal\ mol^{-1}}, \tag{3b}$$

$$\mathrm{NaO} + \mathrm{D_2} \rightarrow \mathrm{NaOD} + \mathrm{D}, \quad \Delta H^\circ_{298} = -16.3 \pm 3\ \mathrm{kcal\ mol^{-1}}, \tag{4a}$$

$$\rightarrow \mathrm{Na} + \mathrm{D_2O}, \quad \Delta H^\circ_{298} = -58.5 \pm 3\ \mathrm{kcal\ mol^{-1}}. \tag{4b}$$

In addition, weak chemiluminescence from channel (3b) was observed. This chemiluminescence was much weaker than the resonant fluorescence signal and did not interfere with the kinetic measurements. As in our previous measurement of NaO + O_3,[10] we can quantitatively measure the rate constants of only the NaO reactions that yield products other than Na, e.g., channels (3a) and (4a). The Na formed in channels (3b) and (4b) reacts with the large excess of N_2O to regenerate NaO. Na formation channels are detected by observing an Na signal with the NO flow turned off. Computer simulations[10] of the flow tube kinetics of an NaO reaction with an Na formation channel have shown that at high [reactant] the k_{obs} vs [reactant] plot will curve down. This was experimentally observed for H_2 and D_2. However, as with NaO + O_3,[10] the simulations show that the k_{obs} vs $[H_2]$ plot will become significantly curved before an inaccurate measurement of k_{3a} would be made. Even when $k_{3a} \approx k_{3b}$, the simulation shows that fitting the linear part of the k_{obs} vs $[H_2]$ plot results in a $<5\%$ underestimate of k_{3a}.

Eighteen measurements of the first-order decay of NaO in the presence of H_2 were made to evaluate k_{3a}. Twenty-four measurements were made to evaluate k_{4a}. Helium was the carrier gas in all the H_2 and D_2 experiments. The kinetic data are summarized in Table I. Figure 1 shows sample k_{obs} vs $[H_2]$ and $[D_2]$ plots. The observed NaO + D_2 → NaOD + D rate constant k_{4a} increases 26% with increasing flow tube velocity over our range of a factor of 3.7. This is undoubtedly due to the perturbing chemistry of reaction (4b). Although we did not obtain any quantitative results, the branching ratio for this channel is apparently greater

TABLE I. Summary of NaO + H_2 and NaO + D_2 kinetic measurements.

p (Torr)	No. of expts.	Mole fraction of N_2O	T (K)	v ($\mathrm{cm\ s^{-1}}$)	[Reactant] (10^{12} $\mathrm{molecule\ cm^{-3}}$)	k_{II}[a] $\pm\ \sigma$ (10^{-11} $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$)
					H_2 reactant	
0.221	6	0.455	294	7250	4.33–17.7	2.80 ± 0.08
0.317	3	0.284	297	7860	2.19–3.93	2.52 ± 0.22
0.320	9	0.263	297	8670	4.09–16.7	2.51 ± 0.08
					Recommended value	(2.6 ± 1.0)[b]
					D_2 reactant	
0.244	6	0.522	295	5230	2.33–9.48	1.26 ± 0.07
0.477	6	0.433	294	3420	2.28–10.3	1.18 ± 0.04
0.853	6	0.389	297	1980	2.90 ± 13.0	1.13 ± 0.03
1.20	6	0.394	298	1420	3.38 ± 22.1	0.997 ± 0.018
					Recommended value	(1.1 ± 0.4)[b]

[a] Obtained from k_{obs} by the method of Brown as described in Sec. II. The standard deviation is from the unweighted least squares fit of the data.

[b] The recommended value includes an estimate of random and systematic errors at the 95% confidence level.

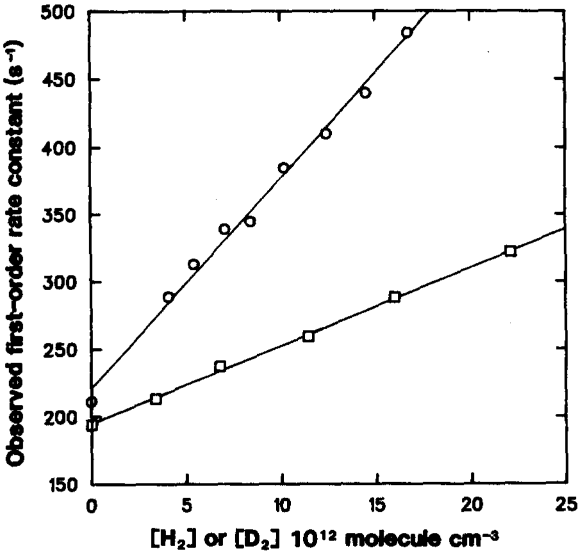

FIG. 1. k_{obs} vs [H_2] and [D_2] for $NaO + H_2 \rightarrow NaOH + H$ and $NaO + D_2 \rightarrow NaOD + D$: (○) H_2 reactant, 0.320 Torr, 297 K, $v = 8670\ cm\ s^{-1}$; (□) D_2 reactant, 1.20 Torr, 298 K, $v = 1420\ cm\ s^{-1}$.

than for the analogous channel in $NaO + O_3$, i.e., $\gtrsim 20\%$. The error limits are larger on these rate constants ($\pm 40\%$) to reflect the greater uncertainties: $k_{3a} = (2.6 \pm 1.0) \times 10^{-11}$ $cm^3\ molecule^{-1}\ s^{-1}$ and $k_{4a} = (1.1 \pm 0.4) \times 10^{-11}$ $cm^3\ molecule^{-1}\ s^{-1}$, both at 296 ± 2 K. The kinetic isotope ratio k_{3a}/k_{4a} is about 2.3.

Since they have no complicating secondary chemistry, the measurements of k_1 and k_5 are comparatively straightforward:

$$NaO + H_2O \rightarrow NaOH + OH, \quad \Delta H^\circ_{298} = -1.4 \pm 3\ \mathrm{kcal\ mol^{-1}}, \tag{1}$$

$$NaO + D_2O \rightarrow NaOD + OD, \quad \Delta H^\circ_{298} = -1.4 \pm 3\ \mathrm{kcal\ mol^{-1}}. \tag{5}$$

Sample decay plots for $NaO + H_2O$ are shown in Fig. 2. The kinetic data in N_2 carrier gas are summarized in Table II. The initial measurements using the the bubbler source and He carrier gas are in excellent agreement. Sample k_{obs} vs [H_2O] and [D_2O] plots are shown in Fig. 3. The measured rate constants show no observable dependence on pressure or velocity. $k_1 = (2.2 \pm 0.4) \times 10^{-10}$ $cm^3\ molecule^{-1}\ s^{-1}$ and $k_5 = (1.2 \pm 0.2) \times 10^{-10}$ $cm^3\ molecule^{-1}\ s^{-1}$ at 298 ± 1 K, where the errors reflect the 95% confidence limits including an estimate of systematic errors. The kinetic isotope ratio k_1/k_5 is 1.8.

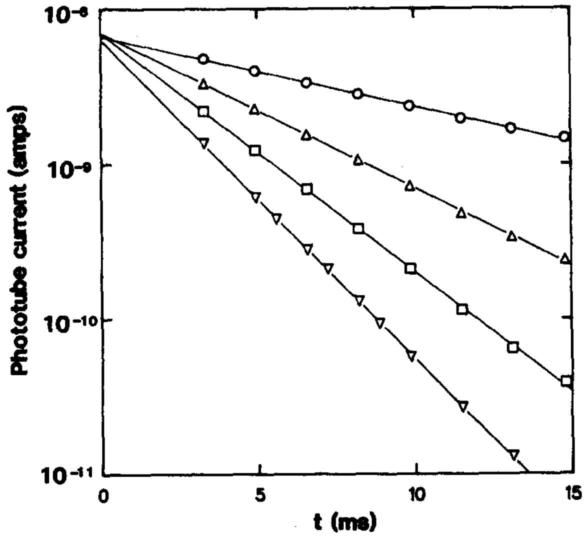

FIG. 2. Sample decay plots for $NaO + H_2O$, 0.507 Torr, $v = 3070\ cm\ s^{-1}$, 299 K: (○) [H_2O] = 0; (△) [H_2O] = 8.46×10^{11} molecule cm^{-3}; (□) [H_2O] = 1.79×10^{12} molecule cm^{-3}; (▽) [H_2O] = 2.80×10^{12} molecule cm^{-3}.

IV. DISCUSSION

We know of no published measurements or estimates of the rate constant for $NaO + H_2$. NaO has a large dipole moment, 8.7 D,[5] corresponding to ~90% ionic character in the bond. Since the anion is the reactive part of the molecule, one might expect the chemical behavior of NaO to be analogous to that of O^-:

$$O^- + H_2 \rightarrow OH^- + H, \quad \Delta H^\circ_{298} = -6.5 \pm 0.5\ \mathrm{kcal\ mol^{-1}}, \tag{6a}$$

$$\rightarrow e + H_2O, \quad \Delta H^\circ_{298} = -83.8 \pm 0.5\ \mathrm{kcal\ mol^{-1}}, \tag{6b}$$

$$O^- + D_2 \rightarrow OD^- + D, \quad \Delta H^\circ_{298} = -6.5 \pm 0.5\ \mathrm{kcal\ mol^{-1}}, \tag{7a}$$

$$\rightarrow e + D_2O, \quad \Delta H^\circ_{298} = -83.8 \pm 0.5\ \mathrm{kcal\ mol^{-1}}. \tag{7b}$$

The analogs of reactions (3) and (4), reactions (6) and (7), have been studied in a flowing afterglow–drift tube experiment.[15] As with $NaO + H_2$, both product channels were observed. At room temperature, the H atom abstraction channel branching ratio was 5%, as opposed to a much larger value for $NaO + H_2$. The abstraction channel increases with ion kinetic energy, becoming roughly equal to the associative detachment channel (6b) for both H_2 and D_2 at center-of-mass kinetic energies around 0.5 eV. The rate constants for channels (6a) and (7a) are 3×10^{-11} and 1.5×10^{-11} $cm^3\ molecule^{-1}\ s^{-1}$ at 300 K, which are very close to the NaO values, k_{3a} and k_{4a}. The kinetic isotope effect k_{6a}/k_{7a} of 2.0 ± 0.5 is also very close to the NaO value of 2.3. In the ion–molecule study,[15] the reaction was postulated to occur in two steps. First, rapid H atom abstraction occurs to form $OH^- + H$. Next, the nascent products undergo associative detachment before they can separate, $OH^- + H \rightarrow e + H_2O$. This explains how O^- can insert into the H_2 bond without a large activation energy. The strong electrostatic forces give the $OH^- \cdot H$ intermediate a sufficiently long lifetime to permit the second channel. It is reasonable that the same type of two-step mechanism is operable for $NaO + H_2$:

$$\begin{array}{c} NaO + H_2 \rightarrow [NaOH \cdot H]^\dagger \rightarrow NaOH + H \\ \downarrow \\ Na + H_2O. \end{array} \tag{8}$$

Although we prefer the above mechanism which is consistent with the observed kinetic isotope effect, it is also possible that the reaction occurs on two separate potential energy

TABLE II. Summary of NaO + H_2O and NaO + D_2O kinetic measurements.

p (Torr)	No. of expts.	Mole fraction of N_2O	T (K)	v ($cm\ s^{-1}$)	[Reactant] (10^{11} molecule cm^{-3})	$k_{II}{}^{a} \pm \sigma$ ($10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$)
				H_2O reactant		
0.287	6	0.349	298	5190	5.96–43.8	2.20 ± 0.01
0.302	7	0.297	298	5200	3.79–53.6	2.22 ± 0.04
0.398	6	0.352	298	3700	3.13–27.1	2.35 ± 0.06
0.507	6	0.308	297	3070	8.46–28.0	2.20 ± 0.04
					Recommended value	$(2.2 \pm 0.4)^b$
				D_2O reactant		
0.360	7	0.352	298	4070	6.77–55.1	1.22 ± 0.05
0.440	7	0.353	298	3310	3.17–38.1	1.21 ± 0.01
0.547	6	0.350	299	2660	4.67–28.5	1.24 ± 0.01
					Recommended value	$(1.2 \pm 0.2)^b$

[a] Obtained from k_{obs} by the method of Brown as described in Sec. II. The standard deviation is from the unweighted least squares fit of the data.

[b] The recommended value includes an estimate of random and systematic errors at the 95% confidence level.

surfaces, one for direct H abstraction and the other for insertion into the H_2 bond.

The consistent results in two carrier gases and the absence of a pressure effect over our pressure range (0.29–0.55 Torr) clearly show that NaO + H_2O is a bimolecular reaction. The kinetic isotope effect suggests that there is significant OH bond breaking in the transition state. Since the reaction is fast, it cannot be strongly endothermic. If we assume it is thermoneutral, we obtain a lower limit on the heat of formation of NaO, $\Delta H^{\circ}_{f,298}$ (NaO)$\geqslant$23.4 kcal mol^{-1}. Although this value is dependent on the measured value for $\Delta H^{\circ}_{f,298}$(NaOH),[9] it is consistent with the experimental and theoretical studies.[4–8] We should note that it is unusual for a radical species to efficiently abstract H atoms from water. The rate constant for NaO + H_2O is about five times faster than F + H_2O and about the same as $O(^1D) + H_2O$.[16]

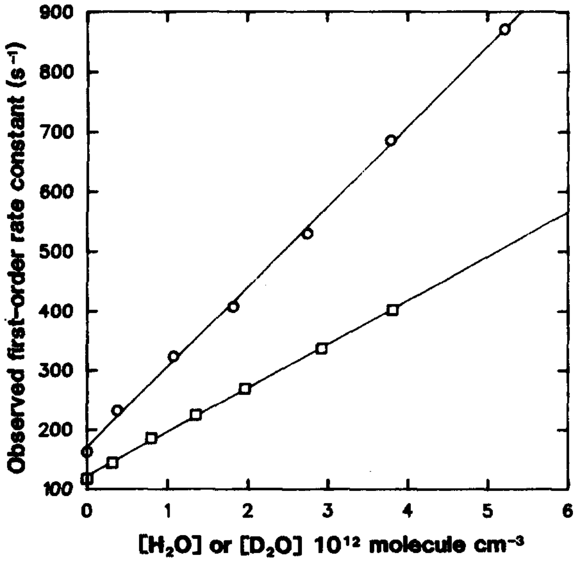

FIG. 3. k_{obs} vs [H_2O] and [D_2O] for NaO + H_2O and NaO + D_2O: (○) H_2O reactant, 0.302 Torr, 298 K, $v = 5200\ cm\ s^{-1}$; (□) D_2O reactant, 0.440 Torr, 298 K, $v = 3310\ cm\ s^{-1}$.

Although reactions (1) and (5) are certainly fast, they are not at the gas kinetic limit. Because of the large dipole moments of NaO (8.7 D)[5] and H_2O (1.85 D),[17] dipole–dipole and dipole–dipole induced dipole forces cause these molecules to have an unusually large collision rate constant. We have estimated the collision rate constant with a simple electrostatic model similar to that described by Clary.[18] The approach is analogous to that used to calculate Langevin rate constants for ion–molecule reactions.[19]

In the present model, we calculate the coefficients of the R^{-6} leading terms in the attractive potential between the two dipoles. We use the orientationally averaged dipole–dipole and dipole–dipole induced dipole formulas and a simple dispersion estimate[20]:

$$C_6(\text{dipole–dipole}) = 4.828\times10^{-57}\,\frac{\mu_1^2\mu_2^2}{T}\ \text{erg cm}^6, \tag{9}$$

$$C_6(\text{dipole–dipole induced dipole}) = 1\times10^{-36}\,(\alpha_1\mu_2^2+\alpha_2\mu_1^2)\ \text{erg cm}^6, \tag{10}$$

$$C_6(\text{dispersion}) = 2.403\times10^{-12}\,\frac{I_1I_2\alpha_1\alpha_2}{(I_1+I_2)}\ \text{erg cm}^6, \tag{11}$$

where μ_i is the dipole moment in Debye, α_i is the polarizability in cm^3, I_i is the ionization potential in eV, the subscripts refer to the two reactants, and T is the temperature in K. The

TABLE III. Collision rate constant calculation for NaO + H_2O.

	NaO	H_2O
μ (D)	8.7^a	1.85^b
α (Å^3)	3.4^c	1.45^d
IP (eV)	6.5^e	12.6^f

[a] Reference 5.

[b] Reference 18.

[c] Reference 10 (estimate).

[d] T. M. Miller, in *Handbook of Chemistry and Physics*, 66th ed., edited by R. C. Weast (Chemical Rubber, Boca Raton, 1985), pp. E-65–E-74.

[e] Reference 4.

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TABLE IV. Calculated C_6 coefficients and the NaO + H_2O collision rate constant.[a]

Force	C_6 (10^{-60} erg cm^6)
Dipole–dipole	4170
Dipole–dipole induced dipole	121
Dispersion	51
Total	4340

[a] $k_{\text{collision}} = 2.0 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.

input parameters for the NaO + H_2O calculation are listed in Table III and the calculated C_6 coefficients are summarized in Table IV. The dipole–dipole term is by far the strongest attractive force. If we now assume that the only repulsive term is the centrifugal barrier, we obtain the rate constant[19]:

$$k_{\text{collision}} = 1.672 \times 10^{10}\, T^{1/6} \mu^{-1/2} C_6^{1/3}\ \text{cm}^3\text{molecule}^{-1}\,\text{s}^{-1}, \quad (12)$$

where μ is the reduced mass in amu. This calculation yields a NaO + H_2O collision rate constant of 2.0×10^{-9} cm^3 molecule^{-1} s^{-1}, which is nearly an order of magnitude larger than the measured reaction rate constant. Note that when the dipole–dipole term is dominant, the collision rate has a very weak $T^{-1/6}$ temperature dependence. Since there is a relatively small difference between the calculated collision rates for H_2O and D_2O, the observed kinetic isotope effect is consistent with a mechanism whose rate is not limited by the collision rate but by the rate of transfer of the H/D atom within the collisional complex.

In the mesosphere, Na, NaO, and NaO_2 are rapidly interconverted by photolysis and reactions involving O, O_2, and O_3.[3] For example, $NaO + O \rightarrow Na + O_2$ is the fastest NaO reaction at 90 km and is the source of the Na *D* line night airglow. The Na formed in this reaction is quickly recycled back to NaO via $Na + O_3 \rightarrow NaO + O_2$. For this reason, reactions (1) and (3) have a special significance in the mesospheric chemistry of Na species since they form NaOH, which does not have a known rapid chemical path back to the reactive species (Na, NaO, NaO_2). Our result for the NaO + H_2O rate constant supports the proposal of Sze *et al.*[3] that NaOH will be the dominant Na species at 80 km. However, we show elsewhere[21] that NaOH will react to form even more stable species at lower altitudes. NaO + H_2 had not been considered previously as a possible source of NaOH. If we assume mole fractions for H_2O and H_2 of 1 and 0.5 ppm at 90 km,[22] the rate of reaction (1) will be 17 times faster than reaction (3a). The mole fraction of water is variable, but is thought to be between 0.5 and 1 ppm at 90 km.[22] The H_2O mole fraction would have to fall significantly below this for reaction (3) to be an important souce of NaOH. We conclude that NaO + H_2O is the major source of NaOH in the mesosphere.

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