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LETTERS

Radical-Molecule Kinetics in Pulsed Uniform Supersonic Flows: Termolecular Association of OH + NO between 90 and 220 K

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The low-temperature dependence of the termolecular association reaction of OH with NO employing N₂ as the third body has been investigated using a new pulsed uniform supersonic expansion flow reactor. The absolute low-pressure reaction rate coefficient is reported for the temperature range 90-220 K. The temperature dependence of the rate coefficient for this reaction is found to be well fit by $k = (7.0 \pm 2.0) \times 10^{-31} (T/300)^{-2.6 \pm 0.3}$ cm⁶ s⁻¹. The results agree with those obtained in the higher temperature regime and with RRKM predictions of the rate coefficient both validating the new technique and providing valuable information on the extended temperature dependence of this atmospherically relevant reaction.

Introduction

The temperature dependence of free radical recombination reactions plays a critical role in the chemical dynamics and composition of planetary atmospheres, including our own.¹⁻³ These reactions often manifest strong inverse temperature dependences, with the reaction rate coefficients increasing with decreasing temperature, or even more complex behavior. Currently, there is strong interest in the chemistry of hydroxyl-containing reservoir species such as nitrous and nitric acid. Nitric acid is specifically thought to be a chain-terminating product in at least one of the ozone depletion reaction cycles due to its stability to oxidation. Furthermore, as a stable form of odd oxygen, it can act as a transport agent for OH in the stratosphere. The impact of strong seasonal variation of the stratospheric temperature over certain parts of the globe demands careful laboratory determination of the rates for reservoir species production reactions across a broadened range of temperatures.

Certainly, two of the most atmospherically relevant association reactions of hydroxyl are those with nitric oxide and nitrogen dioxide:

 $OH + NO + N_2 \rightarrow HONO + N_2$ $\Delta H = -49.87 \text{ kcal/mol} (1)$

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$$OH + NO_2 + N_2 \rightarrow HONO_2 + N_2$$

 $\Delta H = -49.5 \text{ kcal/mol} (2)$

These reactions are also important in combustion processes and have been extensively studied in the elevated to near ambient temperature range (550-230 K).⁴⁻¹⁶ The negative temperature dependence in this window has been well explained using RRKM models.^{15,17,18} These attribute enhanced low-temperature reactivity to the increased lifetime of the initially formed HONO collision complex at low collision energy. As a result, most of the laboratory findings have been fit to a statistical model employing a $k = CT^n$ dependence. Clearly, an extension of the temperature range to much lower temperatures provides a sensitive and valuable test of these models. Additionally, the temperature extant in the upper atmosphere is only approached by the currently available data, and it is necessary to extend the temperature range of laboratory kinetic data well below 230 K.

We have recently developed a new method with the capability of determining absolute rate coefficients for radical-molecule and radical-radical reactions at temperatures between 20 and 300 K. Similar to parallel efforts of Rowe, Smith, and co-workers,^{19,20} low temperatures are produced in our method using pulsed adiabatic expansion of reaction mixtures to fixed Mach numbers in Laval nozzles. The kinetic technique employs the constant density and temperature core of a uniform supersonic flow as the reaction medium. Radicals are produced by cold

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Figure 1. Block diagram of the pulsed uniform supersonic expansion reactor: 1 pulsed valve; 2 nozzle translator; 3, discharge electrode; 4, cooling/heating coils; 5, LIF laser path; 6, LIF image point; 7, LIF camera; 8, impact pressure transducer.

cathode discharge or laser photolysis prior to expansion and are monitored in the post expansion region by laser-induced fluorescence.

In this first report from our group, we present results for the absolute reaction rate coefficients of reaction 1 at temperatures between 90 and 220 K. The results both demonstrate the utility of the new method and support the statistical interpretation of the reaction mechanism in the HONO recombination reaction at low temperature. The new technique provides information which when added to the existing data base completely spans the atmospherically relevant temperature range.

Experimental Section

A detailed description of the pulsed uniform supersonic expansion reactor will be presented in a subsequent publication along with results from studies of the analogous reaction OH + NO₂. Briefly, referring to Figure 1, a pulsed uniform supersonic expansion is produced using a shaped Laval type convergentdivergent nozzle. The flow gas, consisting of 0.5% water vapor, 0-10% NO, and balance N₂ is admitted to the stagnation volume using a 3-mm-orifice pulsed valve (General Valve Series 9, 6-ms duration pulses operating at 10 Hz). Cold cathode discharge in the stagnation zone efficiently generates OH radicals, which are thermally equilibrated during the subsequent expansion. The flow gas is accelerated to a final Mach number at the nozzle exit plane, which remains constant in the post nozzle flow region and is determined by nozzle design. This should be contrasted to free jet expansions where the Mach number is constantly increasing. The implication of constant Mach number is that the flow retains a constant local density and temperature in the flowing frame. It is this particular property of Laval expansions which makes them a favorable medium for kinetic studies at the local conditions. By using laser-induced fluorescence (LIF) or resonantly enhanced multiphoton ionization (REMPI), it is possible to determine the local thermal conditions and monitor reactant or product densities.

TABLE 1: A Summary of the Results for Reaction 1*

	stagnation temp (K)	flow temp (K)	flow density (cm ⁻³)	k ₃ (cm ⁶ /s)
Mach 2	250	139	1.5×10^{17}	4.2×10^{-30}
	300	167	1.4×10^{17}	2.4×10^{-30}
	350	194	1.3 × 10 ¹⁷	2.0×10^{-30}
	400	222	1.2×10^{17}	1.5×10^{-30}
Mach 3	250	89	$6.0 imes 10^{16}$	16×10^{-30}
	300	107	5.5×10^{16}	10×10^{-30}
	350	125	5.1×10^{16}	7.8 × 10 ⁻³⁰

^a All data were fit to $k_1 = (7.0 \pm 2.0) \times 10^{-31} (T/300)^{-2.6 \pm 0.3} \text{ cm}^6 \text{ s}^{-1}$.

In the present study we used a pulsed Nd:YAG pumped dye laser system for optical interrogation (Continuum NY61/ND60/ UVX). In this report, LIF studies of $OH(\tilde{A} \leftarrow \tilde{X})$ were used both to confirm local thermal conditions and to monitor reactant loss rate. Owing to the pulsed nature of the expansion, the 1-cm throat diameter, and the small size of the vacuum chamber, pumping requirements for this experiment are quite modest (Leybold-Heraeus WAU-150 Roots blower, 100 cfm, backed with a Sargent Welch 1374 roughing pump, 35 cfm).

The nozzles were designed using a method of characteristics solution of the isentropic flow with a numerical correction for viscous boundary layer effects.^{21,22} The pressure in the Mach 1 throat (see Figure 1) is on the order of 10 Torr, depending on stagnation temperature and final design Mach number. This study reports results obtained using two nozzles, final Mach numbers 2 and 3. A particular nozzle gives one final Mach number flow which corresponds to a certain degree of cooling and density drop by the well-known one-dimensional relationships²³

$$\frac{T}{T_0} = \left(1 + \frac{\gamma - 1}{2}M^2\right)^{-1}$$
(3)

$$\frac{\rho}{\rho_0} = \left(1 + \frac{\gamma - 1}{2}M^2\right)^{-1/(\gamma - 1)}$$
(4)

where T and ρ are temperature and density in the final flowing frame, T_0 and ρ_0 correspond to stagnation conditions, γ is the heat capacity ratio for the flow gas, and M is the design Mach number. The stagnation temperature of the expansion is varied from 250 to 400 K using a thermostated liquid circulating system. With these stagnation temperatures the two different Mach number nozzles access a flow temperature range from 90 to 220 K as summarized in Table 1.

Initial flow characterization is performed by measuring impact pressures on a small pressure transducer mounted on a Cartesian carriage (Omega PX-136). The uniform flow density persists at the 90% level for a distance of 10-15 cm as determined by impact pressure measurements and LIF. Figure 2 illustrates impact pressure measurements obtained for the Mach 3 nozzle at 300 K, demonstrating the uniform axisymmetric nature of the flow. The effects of viscosity and thermal transfer limit the distance over which we obtain uniform flow and cause the broadening seen in the radial scans. Interestingly, flow uniformity is also a sensitive function of background gas pressure (in the chamber) which must be adjusted for each nozzle/stagnation temperature and is determined by a capacitance manometer.

Results and Discussion

For the hydroxyl radical reactions reported here, a cold cathode discharge in a water vapor seeded flow was found to be a useful OH production method, producing copious quantities of the radical. At the nozzle exit, the OH was found by LIF to reside only in the lowest energy states, OH $\tilde{X}^2 \Pi_{1/2,3/2}(v=0)$. Clearly, collisions with water vapor and the buffer during the expansion process effectively cool the nascent OH. Rotationally resolved excitation spectra of the R₁ and R₂₁ branches of the (0,0) band



Figure 2. Radical scans of the impact pressure of the flow. The circles, squares, and diamonds represent the scan at 0, 5.5, and 11.5 cm from the nozzle exit, respectively.



Figure 3. Temperature dependence of the low-pressure termolecular rate coefficient for reaction 1, $OH + NO + N_2 \rightarrow HONO + N_2$, from 90 to 550 K. The shaded region represents the recommendation of DeMore *et al.* (ref 15).

of the $\tilde{A} \leftarrow \tilde{X}$ transition displayed rotational distributions well fit to temperatures consistent with those predicted by the isentropic relationship for both nozzles (eq 3). All of the assignments for OH are from the paper by Dieke and Crosswhite.²⁴ This fact demonstrates that the flows exhibit thermal equilibrium between all degrees of freedom owing to the continuum nature of the flow. The OH density, monitored by observing the $R_1(2)$ line near 307 nm, was also found to be constant within 5% in the absence of added reactant, again demonstrating the uniform nature of the flow (at least on the center steam line). As small fractions of NO are seeded into the flow, the OH LIF signal was observed to decrease with distance in a pseudo-first-order manner. The observed rate was found to increase linearly with increasing NO concentration, allowing extraction of the absolute rate coefficient at a given total flow pressure. By maintaining relative NO fractions below 10%, the third body was nitrogen in the 10¹⁶-1018-cm-3 density range. Under these conditions, the reaction is in the low-pressure limit, and the low-pressure absolute reaction rate coefficients are summarized in Table 1.

Figure 3 shows the termolecular association rate coefficient versus temperature for reaction 1 between 90 and 550 K. The shaded region represents the recommended temperature dependence of the rate coefficient including error from deMore *et al.*¹⁵ The good agreement between our low-temperature measurements and the recommendation addresses several issues. First, it would appear that the new technique reported here provides reliable rate coefficient information in the low-temperature regime, not easily accessible via conventional kinetic methods. Second, it is evident that simple statistical interpretations of the reaction



Figure 4. New recommended temperature dependence of the rate coefficient for reaction 1, where the shaded region represents the uncertainty (2σ) . The filled circles represent new data from this report, while the filled square represents an average of values at 300 K reported by DeMore *et al.* (ref 15).

mechanism remain valid at low temperatures as manifested by the inverse power dependence of k_3 on temperature. Combining the new results with the high-temperature recommendation allows us to report a global temperature dependence for the termolecular association reaction. The new recommendation is $k_1 = (7.0 \pm 2.0) \times 10^{-31} (T/300)^{-2.6\pm0.3}$ cm⁶ s⁻¹ between 90 and 550 K. Figure 4 shows the new recommendation for the rate coefficient and the error bars associated with it. Extrapolation of the recommendation of Atkinson,¹⁸ based on data obtained above 200 K, $k_1 = 7.0 \times 10^{-31} (T/300)^{-2.4\pm0.5}$ cm⁶ s⁻¹, is nearly coincident with the new recommendation, but the error limits on the temperature dependence have significantly contracted due to the extension of the experimental temperature range.

Conclusions

In this study we have demonstrated our approach to lowtemperature kinetic studies using the termolecular recombination of nitrous acid as a benchmark. The good agreement of the temperature dependence of the reaction rate coefficient of the termolecular association reaction $OH + NO + N_2 \rightarrow HONO +$ N_2 with recommended high-temperature results is not surprising for this benchmark and helps to validate this low-temperature technique. The data presented here help to support the validity of the RRKM approach to explaining the enhanced reactivity of small barrierless reactions on the basis of collision complex lifetime enhancement.

The use of pulsed uniform supersonic flows shows great promise for extension of radical-molecule and radical-radical reaction rate studies into the low-temperature regime. Currently, new Mach number nozzles are being developed in our laboratory which extend both the low- and high-temperature limits reported in this study. The technique, it should also be stressed, is equally applicable to bimolecular reactions, and further investigations of both types of reactions are currently in progress.

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