Enhancement of the $NH_2 + NO \rightarrow OH + H + N_2$ Reaction by Vibrational Excitation of NH_2

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The reaction of amino radical (NH_2) with nitric oxide (NO) has attracted the attention of researchers engaged in atmospheric and combustion chemistry. The fate of NH_2, generated in the atmosphere by $OH + NH_3 \rightarrow NH_2 + H_2O$, is governed by the reaction with the trace species NO, particularly in the urban areas. The $DeNO_x$ process, which is the noncatalytic reduction of NO_x by NH_3 in power plants, is based on the NH_2 + NO reaction. There are three exothermic channels in the reaction of NH_2 with NO:

$$NH_2 + NO \rightarrow OH + H + N_2 \qquad \Delta_r H^\circ_{298} = -24 \text{ kJ mol}^{-1} \qquad (1)$$

$$\rightarrow N_2O + H_2 \qquad \Delta_r H^\circ_{298} = -199 \text{ kJ mol}^{-1} \qquad (2)$$

$$\rightarrow H_2O + N_2 \qquad \Delta_r H^\circ_{298} = -522 \text{ kJ mol}^{-1} \qquad (3)$$

Marcy et al.[1] reported that N_2O via channel 2 is produced from vibrationally excited NH_2 and H_2O in channel 3 is generated by vibrationally relaxed NH_2. In this paper, the authors have studied the effect of vibrational excitation of NH_2 on channel 1.

A gaseous mixture of NH_3(0.5–30 mTorr)/NO(5–100 mTorr)/He(5–100 Torr) in a flow cell at 298 K was irradiated with an ArF laser (193 nm) to initiate NH_2 + NO. $NH_2(\tilde{X}^2B_1)$ and $OH(X^2\Pi, v = 0)$ were detected with laser-induced fluorescence (LIF) via the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ and $A^2\Sigma^+ - X^2\Pi$ transitions, respectively, and H atoms with Lyman-α radiation following two-photon excitation at 243 nm. Time-resolved LIF intensities of the three species were recorded as a function of the delay times between the photolysis and probe lasers under the conditions of various partial pressures. We also have added CF_4 which is an efficient relaxation partner of NH_2 and an inefficient quencher of $OH(A^2\Sigma^+)$, finding the significant reduction of the yield of OH with an increase in CF_4 as shown in Figure 1. The results indicate that channel 1 is enhanced by vibrational excitation of NH_2.

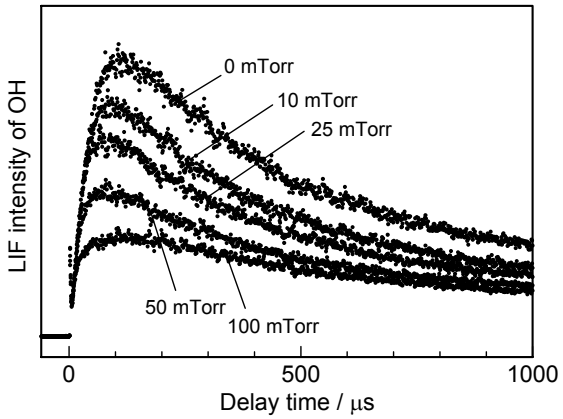

Figure 1. Time-resolved LIF intensities of $OH(X^2\Pi, v = 0)$ recorded at different pressures of CF_4. $p_{NH_3} = 0.5$ mTorr, $p_{NO} = 5$ mTorr, $p_{He} = 5$ Torr.

References

(1) Marcy, T. P.; Heard, D. E.; Leone, S. R. *J. Phys. Chem. A* **2002**, 106, 8249-8255.

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