Determination of the Rate Constants for the $NH_2(X^2B_1)$ + $NH_2(X^2B_1)$ and $NH_2(X^2B_1)$ + H Recombination Reactions with Collision Partners CH_4, C_2H_6, CO_2, CF_4, and SF_6 at Low Pressures and 296 K

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The recombination rate constants for the reactions $NH_2(X^2B_1)$ + $NH_2(X^2B_1)$ + M and $NH_2(X^2B_1)$ + H +M, where M was CH_4, C_2H_6, CO_2, CF_4, or SF_6, were measured in the same experiment over the pressure range 1 to 20 Torr and 7 to 20 Torr, respectively, at 296±2 K. The NH_2 radical was produced by the 193 nm laser photolysis of NH_3. Both NH_2 and NH_3 were monitored simultaneously following the photolysis laser pulse. High-resolution time-resolved absorption spectroscopy was used to monitor the temporal dependence of both species: NH_2 on the $^12_{21} \leftarrow {}^13_{31}$ rotational transition of the $(0,7,0)A^2A_1 \leftarrow (0,0,0)X^2B_1$ electronic transition near 675 nm and NH_3 in the IR on either of the inversion doublets of the $^qQ_3(3)$ rotational transition of the ν_1 fundamental near 2999 nm. The NH_2 self-recombination clearly exhibited fall-off behavior for the third-body collision partners used in this work. The pressure dependences of the NH_2 self-recombination rate constants were fit using Troe's parameterization scheme, k_{inf}, k_0, and F_{cent}, with $k_{inf} = 7.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, the theoretical value calculated by Klippenstein et al.[(1)] The individual Troe parameters were: CH_4, $k_0^{CH_4} = 9.4 \times 10^{-29}$ and $F_{cent}^{CH_4} = 0.61$; C_2H_6, $k_0^{C_2H_6} = 1.5 \times 10^{-28}$ and $F_{cent}^{C_2H_6} = 0.80$; CO_2, = $k_0^{CO_2}$ 8.6×10^{-29} and $F_{cent}^{CO_2} = 0.66$; CF_4, $k_0^{CF_4} = 1.1 \times 10^{-28}$ and $F_{cent}^{CF_4} = 0.55$; SF_6, $k_0^{SF_6} = 1.9 \times 10^{-28}$ and $F_{cent}^{SF_6} = 0.52$, where the units of k_0 are cm^6 moleule^{-2} s^{-1}. The NH_2 + H + M reaction rate constant was assumed to be in the three-body pressure regime, and the association rate constants were: CH_4, (6.0×10^{-30}); C_2H_6, (1.1×10^{-29}); CO_2, $(6.5 \pm 1.8) \times 10^{-30}$; CF_4, $(8.3 \pm 1.7) \times 10^{-30}$; SF_6, $(1.4 \pm 0.30) \times 10^{-29}$, with units cm^6 molecule^{-1} s^{-1}, and the systematic and experimental errors are given at the 2σ confidence level

References

(1) J. Phys. Chem A. **113**, *113*, 10241

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