

# Theoretical Study of H(D) + N<sub>2</sub>O: Effects of Pressure, Temperature, and Quantum-Mechanical Tunneling on H(D)-Atom Decay and OH(D)-Radical Production

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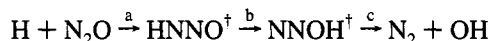
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RRKM calculations based on the theoretical BAC-MP4 potential energy data and molecular parameters for H(D) + N<sub>2</sub>O reactions have been carried out by solving master equations which incorporate tunneling effect corrections for the H-atom (or D-atom) addition and migration processes. The generalized reaction mechanism involves an energetic adduct (HNNO<sup>†</sup> or DNNO<sup>†</sup>), which can redissociate back to the reactants, undergo an H-atom (or D-atom) migration to form products, or it could be stabilized via collisional deactivation. The thermal rate coefficients for the unimolecular decomposition and bimolecular chemical activation according to this mechanism were obtained from the numerical solution of master equations based on the Nesbet algorithm, microscopic reversibility, and Gaussian elimination, with the weak collision assumption using the exponential-down model. The convoluted effect of pressure and tunneling accounts for the observed curvature in the Arrhenius plots for the reactions of both H and D atoms. The calculated results are in excellent agreement with the experimental data of Marshall et al. (*J. Phys. Chem.* 1989, 93, 1922).

## Introduction

The reaction of H atoms with N<sub>2</sub>O is relevant not only to the H<sub>2</sub>-N<sub>2</sub>O flame chemistry but also to the kinetics of NO<sub>x</sub> reduction with NH<sub>3</sub><sup>1</sup> and HNCO,<sup>2</sup> in which the NH + NO reaction, producing H + N<sub>2</sub>O and N<sub>2</sub> + OH products, plays a significant role in NO removal.<sup>3–5</sup>

The kinetics of the H + N<sub>2</sub>O reaction have been studied in detail by Marshall et al.,<sup>6,7</sup> including the observation of a noticeable kinetic isotope effect at low temperatures.<sup>7</sup> On the basis of the result of a potential energy surface calculation by Melius<sup>6</sup> with the bond-additivity corrected Møller–Plesset fourth-order perturbation (BAC-MP4) method,<sup>8,9</sup> Marshall et al.<sup>7</sup> attributed the nonlinear Arrhenius behavior of H-atom decay rates observed at lower temperatures (400–700 K) to the effect of quantum-mechanical tunneling on the H-atom migration process (b), following initial addition to the terminal N atom:



The transition states (TSs) for all three steps (a)–(c) have been calculated by Melius with the BAC-MP4 method as referenced above and, more recently, by Walch<sup>10</sup> and Durant<sup>11</sup> in relation to the NH + NO reaction, which, as mentioned above, is known to produce H + N<sub>2</sub>O and N<sub>2</sub> + OH via TS (a) and TSs (b and c), respectively. These TSs are, therefore, theoretically well characterized.

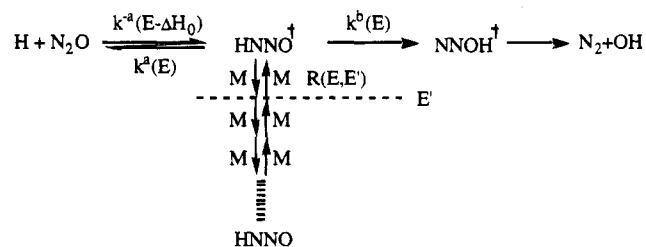
In the present study, we examine the effects of pressure, temperature, and quantum-mechanical tunneling on the lifetime of the chemically activated HNNO intermediate formed by the initial addition reaction, H + N<sub>2</sub>O → HNNO<sup>†</sup>. On account of the presence of a relatively large potential well (~15 kcal mol<sup>-1</sup>) and the high barrier for H-atom migration (~15 kcal mol<sup>-1</sup> from the reactants), the effect of pressure on the stabilization and the tunneling of the excited HNNO<sup>†</sup> may be significant. To our knowledge, the calculation of tunneling probability involving partially deactivated excited molecules as a function of pressure and temperature has not yet been performed. This calculation requires a reliable estimate of the internal energy distribution

of the HNNO<sup>†</sup> molecules at a specific temperature and pressure, because tunneling probability depends strongly on the energy of the molecules.

## Computation Procedure

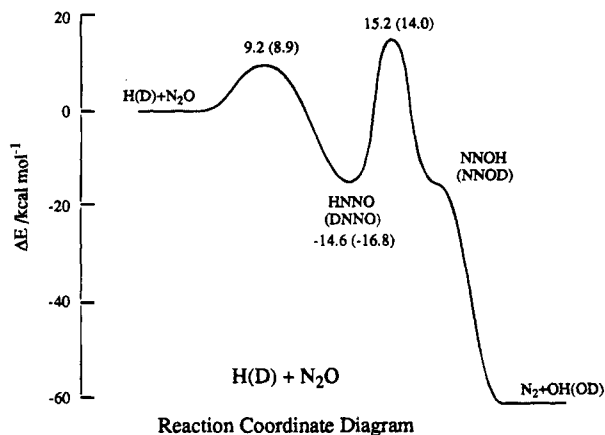
According to the results of previous ab initio calculations,<sup>6,8–11</sup> the reaction of H atom (or D atom) and N<sub>2</sub>O involves an energy barrier of about 9 kcal mol<sup>-1</sup> to form the vibrationally excited intermediate HNNO<sup>†</sup> (or DNNO<sup>†</sup>), which undergoes a 1,3-hydrogen (or 1,3-deuterium) shift with a barrier (~15 kcal mol<sup>-1</sup> for HNNO<sup>†</sup> or ~14 kcal mol<sup>-1</sup> for DNNO<sup>†</sup>) to give a NNOH (or NNOD) species. The latter is unstable and dissociates into N<sub>2</sub> + OH (or OD). The reaction coordinate diagram based on the BAC-MP4 method is shown in Figure 1, where the numbers represent the calculated energies relative to reactants at 0 K (isotope results are shown in parentheses).

The Rice–Ramsperger–Kassel–Marcus (RRKM) calculations for the H(D) + N<sub>2</sub>O reactions were performed by solving the master equation<sup>12,13</sup> for the system. The reaction mechanism involving multiple vibrational energy transfer for the excited intermediate is indicated in the following scheme (for simplicity, the similar scheme for D + N<sub>2</sub>O is not shown here):



where “†” represents internal excitation. Here  $\Delta H_0$  is the enthalpy difference between the reactants (H + N<sub>2</sub>O) and the intermediate (HNNO) at 0 K,  $k^a(E)$  and  $k^b(E)$  are the microscopic rate coefficients at energy  $E$  for the unimolecular dissociation of the excited intermediate (HNNO<sup>†</sup>) via channels (a) and (b) to form the reactants and the products (N<sub>2</sub> + OH), respectively,  $k^{-a}(E - \Delta H_0)$  is the microscopic bimolecular rate coefficient for formation of the excited intermediate at energy  $E$  from the

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, April 1, 1995.



**Figure 1.** Energy diagram for the H + N<sub>2</sub>O reaction based on the result of BAC-MP4 calculations including zero-point energies.<sup>6-9</sup> The energy values shown in parentheses are for D + N<sub>2</sub>O reaction.

reactants, and  $R(E, E')$  is the rate coefficient of energy transfer by collision for the excited intermediate with the bath gas (M) from  $E'$  to  $E$ . Thus, the master equation for the system is written as

$$\partial g(E, t) / \partial t = [M] \int [R(E, E') g(E', t) - R(E', E) g(E, t)] dE' - [k^a(E) + k^b(E)] g(E, t) + k^{-a}(E - \Delta H_0) f_r(E - \Delta H_0) A(t) B(t) \quad (1)$$

where  $g(E, t)$  represents the population of the excited intermediate HNNO<sup>†</sup> with energy  $E$  at time  $t$ ,  $f_r(E - \Delta H_0)$  is the Boltzmann distribution of energies for the reactants H and N<sub>2</sub>O,  $A(t)$  and  $B(t)$  stand for the concentration of the reactants H and N<sub>2</sub>O, respectively, at time  $t$ . To solve eq 1 mathematically, the product of  $k^{-a}(E - \Delta H_0)$  and  $f_r(E - \Delta H_0)$  would be replaced by  $K_{eq} k^a(E) f(E)$  based on the principle of microscopic reversibility at equilibrium,<sup>13,14</sup> where  $K_{eq}$  is the equilibrium constant for reactants and intermediate, and  $f(E)$  is the thermal distribution function of the excited intermediate HNNO<sup>†</sup> with energy  $E$ . Thus, by the usual rule of matrix multiplication, eq 1 can be simply recast into a discrete form:

$$dg(t)/dt = Jg(t) + K_{eq} k^a(E) f(E) A(t) B(t) \quad (2)$$

where  $J$  is a matrix of microscopic rate coefficients involving energy transfers and reactions for HNNO<sup>†</sup>. The details of the solution for eq 2 can be found in the textbook on unimolecular reactions by Gilbert and Smith,<sup>15</sup> hence, only a summary is given here.

The total thermal rate coefficient for the H + N<sub>2</sub>O reaction (denoted by  $k_{tot}$ ) is determined from the addition and decomposition channels:

$$k_{tot} = k_{add} + k_{dec} \quad (3)$$

where  $k_{add}$  and  $k_{dec}$  are thermal rate coefficients for the reaction of H and N<sub>2</sub>O to form the stable adduct (HNNO) and the final products (N<sub>2</sub> + OH), respectively. According to the principle of microscopic reversibility,  $k_{add}$  can be expressed as

$$k_{add} = K_{eq} k_{uni}^a f_{ne} \quad (4)$$

where  $f_{ne}$  is the nonequilibrium factor, and  $k_{uni}^a$  is the thermal rate coefficient for the unimolecular decomposition of HNNO back to form the reactants via channel (a). Both  $f_{ne}$  and  $k_{uni}^a$  can be formalized as follows:<sup>13-15</sup>

$$f_{ne} = [\int x(E) dE]^2 / \int [x(E)^2 / f(E)] dE \quad (5)$$

$$k_{uni}^a = \int k^a(E) x(E) dE / \int x(E) dE \quad (6)$$

where  $x(E)$ , the nonequilibrium population of HNNO<sup>†</sup> at energy  $E$ , can be obtained from the solution of the master equation described in eq 1 but without consideration of the bimolecular association:<sup>14</sup>

$$-k_{uni} x(E) = \omega \int [P(E, E') x(E') - P(E', E) x(E)] dE' - k(E) x(E) \quad (7)$$

where  $k_{uni} = k_{uni}^a + k_{uni}^b$  and  $k(E) = k^a(E) + k^b(E)$ .  $\omega$  is the collision frequency of HNNO<sup>†</sup> with bath gas,  $P(E, E')$  is the probability of energy transfer for HNNO colliding with bath gas from energy  $E'$  to energy  $E$ . Note that  $P(E, E')$  and  $R(E, E')$  are related by the formula  $\omega P(E, E') = [M] R(E, E')$ .

Equation 7 could be solved by the numerical method based on the Nesbet algorithm,<sup>15,16</sup> with "exponential-down model" used in the probability distribution function. The probability for the down transitions has the exponential expression as follows:<sup>12,15</sup>

$$P(E', E) = \frac{1}{N(E)} \exp\left(-\frac{E - E'}{\alpha}\right), \quad E \geq E' \quad (8)$$

where  $N(E)$  is the normalizing factor, and  $\alpha$ , the energy independent constant, was reasonably assumed to be 1 kcal mol<sup>-1</sup> for both HNNO<sup>†</sup> and DNNO<sup>†</sup> in all calculations.<sup>17</sup> Again, the principle of microscopic reversibility has been applied to obtain the probability for the up transitions:<sup>15</sup>

$$P(E', E) = P(E, E') f(E') / f(E), \quad E < E' \quad (9)$$

To solve the master equation numerically, eq 7 was recast into a discrete form:

$$-k_{uni} x_i = \omega \delta E \sum_j (P_{ij} x_j - P_{ji} x_i) - k_i x_i \quad (10)$$

where  $k_i = k(E)$ , etc.

The strong collision model was used as an initial estimate to solve eq 10 iteratively. For each iteration, the total thermal unimolecular rate coefficient,  $k_{uni}$ , can be evaluated according to eq 6 with an improved distribution function which was obtained from the previous iterative step. The entire procedure is then repeated until the calculated value of  $k_{uni}$  does not change within a desired tolerance. The grain size ( $\delta E$ ) used in the summation of eq 10 was set to 0.5 kcal, which is sufficiently small that the value of  $k_{uni}$  is independent of  $\delta E$ . The upper bound of the summation applied in eq 10 was fixed at 100 kcal for all calculations.

The thermal rate coefficient of formation of N<sub>2</sub> + OH from H + N<sub>2</sub>O,  $k_{dec}$ , could be obtained by the distribution average of  $k^b(E)$  with the steady-state population of HNNO<sup>†</sup>, which can be acquired from the solution in eq 2:

$$k_{dec} = k_{ss} - k_{add} k_{uni}^b / k_{uni} \quad (11)$$

where  $k_{ss}$  is the steady-state thermal rate coefficient for the chemical activation system, which can be formulated as

$$k_{ss} = K_{eq} \int k^b(E) \eta(E) dE \quad (12)$$

where  $\eta(E)$  represents the steady-state distribution function at energy  $E$ , which could be determined from the equation<sup>13-15</sup>

**TABLE 1: Molecular and Transition-State Parameters Used in the RRKM Calculation<sup>a,b</sup>**

species or transition states	$\Delta E^\ddagger/\text{kcal mol}^{-1}$	$I_a, I_b, I_c/\text{amu}$	$\nu_i^{d,e}/\text{cm}^{-1}$
H(D) + N <sub>2</sub> O	0	137.9	615(2), 1244, 2351
H + N <sub>2</sub> O $\rightarrow$ HNNO	9.2 (9.2, <sup>f</sup> 10.3 <sup>g</sup> )	9.7, 147.9, 157.6	1287i, 375, 669(2) 1174, 1829
D + N <sub>2</sub> O $\rightarrow$ DNNO	8.9	16.9, 156.2, 173.1	999i, 307, 611(2) 1162, 1816
HNNO	-14.6 (-14.4, <sup>f</sup> -14.5 <sup>g</sup> )	13.1, 137.2, 150.3	312, 937(2), 1376(2) 3210
DNNO	-16.8	17.5, 141.6, 158.8	300, 901(3), 1428 2346
HNNO $\rightarrow$ N <sub>2</sub> + OH	15.2 (16.6, <sup>f</sup> 16.3 <sup>g</sup> )	30.2, 103.0, 133.2	2427i, 481, 879(2) 1280, 1769
DNNO $\rightarrow$ N <sub>2</sub> + OD	14.0	34.8, 103.0, 137.8	1767i, 480, 767(2) 1255, 1301

<sup>a</sup> The energies, moments of inertia, and vibrational frequencies given for chemical reactions represent those of the transition states involved. <sup>b</sup> The values of collision frequency ( $\omega$ ) for HNNO (or DNNO) with Ar are predicted using the estimated Lennard-Jones parameters:  $\sigma \approx 4 \text{ \AA}$ ;  $\epsilon \approx 150 \text{ K}$ . <sup>c</sup> The energy values are relative to those of reactants with zero-point energy corrections involved. <sup>d</sup> All vibration frequencies of intermediates and transition states have been grouped into four classes by geometric average with degeneracy in parentheses. <sup>e</sup> Imaginary vibrational frequencies express those of the reaction coordinate involved. <sup>f</sup> G2 energy by Durant.<sup>11</sup> <sup>g</sup> CASSCF/CCI energy by Walch.<sup>10</sup>

$$-k^b(E) f(E) = \omega \int [P(E, E') \eta(E') - P(E', E) \eta(E)] dE' - k(E) \eta(E) \quad (13)$$

If the integration form is replaced by a discrete summation notation with a small grain size  $\delta E$ , eq 13 becomes a set of linear simultaneous equations, which can be solved exactly by Gaussian elimination.<sup>18</sup> Since all the rate coefficients located in the last term of eq 11 can be obtained from the solution of eq 10 incorporating eqs 4–6, thus  $k_{\text{add}}$ ,  $k_{\text{dec}}$ , and  $k_{\text{tot}}$  for H(D) + N<sub>2</sub>O reactions can be calculated for various pressures and temperatures by repeating the procedure described above.

The microscopic rate coefficient is defined as

$$k^i(E) = \frac{W_i^\ddagger(E)}{h\rho(E)}, \quad i = a \text{ or } b \quad (14)$$

Here  $\rho(E)$  is the density of states for the intermediate at energy  $E$ ,  $h$  is Planck's constant, and  $W_i^\ddagger(E)$  is the sum of states for the transition state at energy  $E$ , for  $i = a$  or  $b$ , with respective to TS(a) or TS(b). In the general expression with tunneling corrections,<sup>19,20</sup>

$$W^\ddagger(E) = \int_0^E P(\epsilon) Q^\ddagger(E - \epsilon) d\epsilon \quad (15)$$

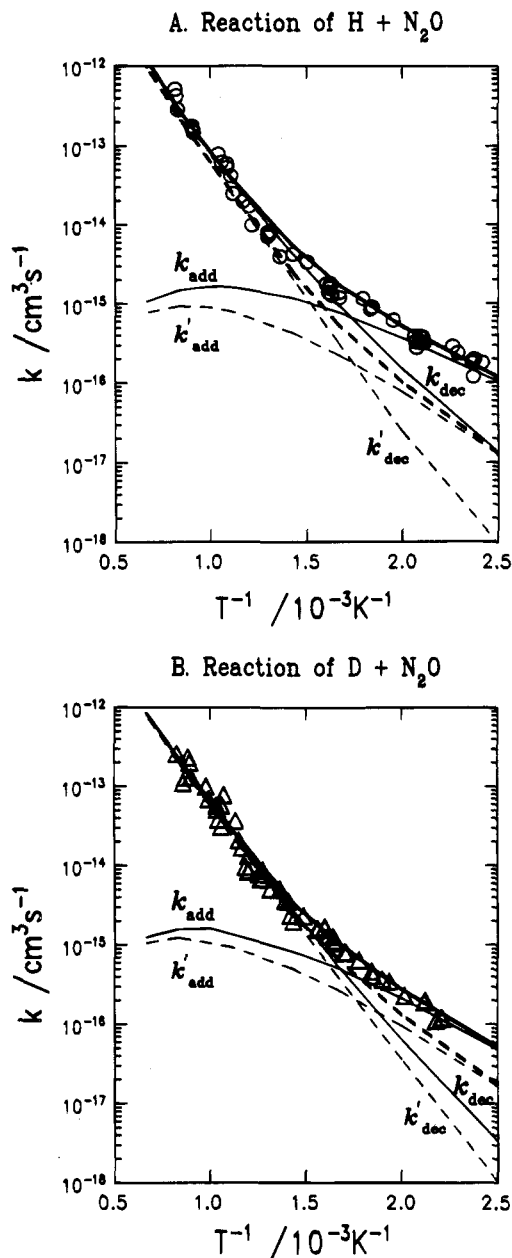
where  $\ddagger$  represents transition-state quantities,  $P(\epsilon)$ , the one-dimensional tunneling probability as a function of the translational energy  $\epsilon$  along the reaction coordinate, can be calculated by fitting a generalized Eckart potential<sup>21</sup> to the potential energy surface for this reaction:<sup>20,22</sup>

$$P(\epsilon) = \frac{\sinh(a) \sinh(b)}{\sinh^2\left(\frac{a+b}{2}\right) + \cosh^2(c)} \quad (16)$$

with

$$a = \frac{4\pi}{h\nu^*}(\epsilon)^{1/2}(V_0^{-1/2} + V_1^{-1/2})^{-1}$$

$$b = \frac{4\pi}{h\nu^*}(\epsilon + V_1 - V_0)^{1/2}(V_0^{-1/2} + V_1^{-1/2})^{-1}$$

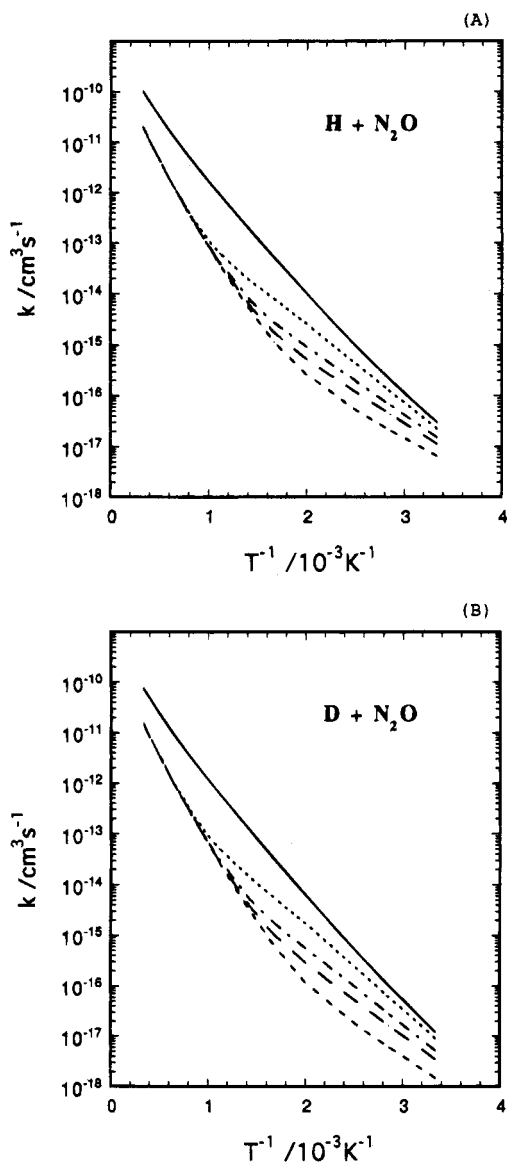


**Figure 2.** Comparison of RRKM results (curves) with experimental data (points) of Marshall et al. for (A) H + N<sub>2</sub>O and (B) D + N<sub>2</sub>O, respectively. Solid and dashed curves are the results of RRKM calculations at 200 Torr with and without tunneling corrections, respectively, and the calculated total rate coefficients represented by bold curves.

$$c = 2\pi \left[ \frac{V_0 V_1}{(h\nu^*)^2} - \frac{1}{16} \right]^{1/2}$$

where  $\nu^*$  is the magnitude of the imaginary frequency related to TS(a) or TS(b),  $V_0$  and  $V_1$  are respectively the barrier height of the corresponding TS (a or b) relative to intermediate and reactants [via TS(a)] or products [via TS(b)]. Note that in the case where  $V_0$  is greater than  $V_1$ , the intermediate cannot get any chance to tunnel through the barrier with energy  $\epsilon$  lower than  $(V_0 - V_1)$ . Therefore, the calculation procedure for the integration in eq 15 is done by summing over the product of  $P(\epsilon)$  and  $Q^\ddagger(E - \epsilon)$  with a small grain size  $\delta\epsilon$ , with  $(V_0 - V_1)$  instead of 0 as an initial summation step if  $V_0 > V_1$ .

The density of states for all of the intermediates and TSs are obtained from the first derivative of the corresponding functions of sum of states, which can be determined by polynomial curve



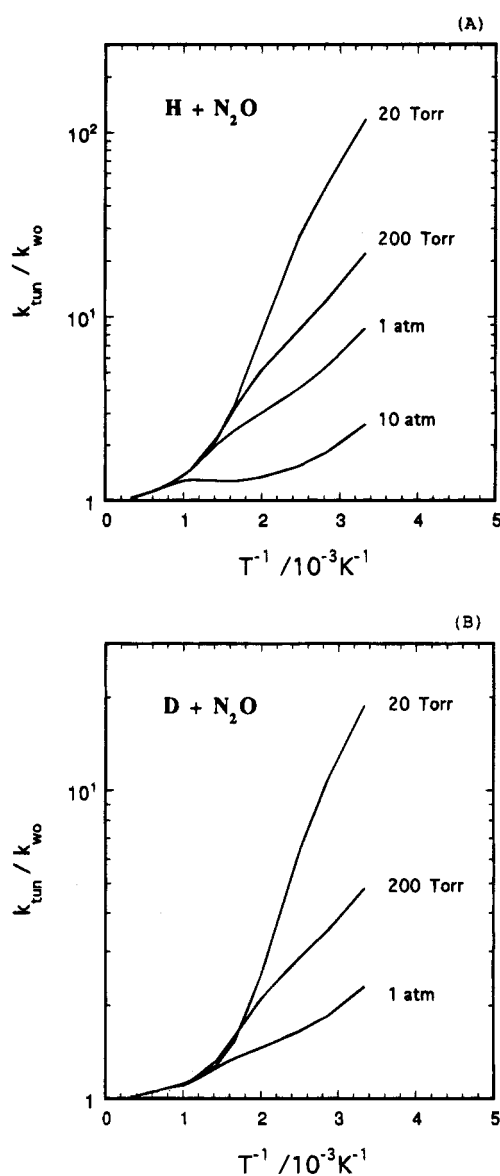
**Figure 3.** Arrhenius plots of total rate coefficients at various pressures for (A) H + N<sub>2</sub>O and (B) D + N<sub>2</sub>O. The pressures are expressed as (---) 20 Torr; (- - -) 200 Torr; (- · -) 1 atm; (···) 10 atm; (—) infinity.

fitting ( $n = 4-7$ , typically) of the results calculated by the direct counting method with vibrational frequencies geometrically averaged into four groups (shown as last column of Table 1) if total energy  $E \leq 30$  kcal (or by the analytical method of Whitten and Rabinovitch<sup>23</sup> if  $E > 30$  kcal).

Table 1 lists the BAC-MP4 parameters of the reactants, intermediates, and TSs used in the RRKM calculations for both H + N<sub>2</sub>O and D + N<sub>2</sub>O reactions. The energies calculated by the complete active space self-consistent field/internally contracted configuration interaction (CASCF/CCI) method<sup>10</sup> and those optimized at the Gaussian-2 (G2) level<sup>11</sup> are included in parentheses for comparison. They are in good agreement. However, no isotope results were provided except the ones with the BAC-MP4 method.

## Results and Discussion

A comparison of total rate coefficients between experiment and theory is shown in Figure 2A,B for the reactions H + N<sub>2</sub>O and D + N<sub>2</sub>O, respectively. All the points (○ for H + N<sub>2</sub>O; △ for D + N<sub>2</sub>O) are the experimental data obtained from the flash-photolysis experiment by Marshall et al.<sup>7</sup> Solid and dashed



**Figure 4.** Plots of tunneling effect at various pressures as indicated, for (A) H + N<sub>2</sub>O and (B) D + N<sub>2</sub>O, respectively.  $k_{\text{tun}}$  and  $k_{\text{wo}}$  are the total rate coefficients with and without tunneling corrections, respectively.

curves are the results of RRKM calculations at 200 Torr with and without tunneling corrections, respectively, in both Figure 2A,B.  $k_{\text{add}}$  (or  $k'_{\text{add}}$  without tunneling corrections) is the addition rate coefficient for H(D) + N<sub>2</sub>O forming the HNNO (DNNO) intermediate, and  $k_{\text{dec}}$  (or  $k'_{\text{dec}}$  without tunneling corrections) is the decomposition rate coefficient for N<sub>2</sub> and OH(OD) production. Thus, the total rate constant (shown as bold curves in both figures) is equal to the sum of  $k_{\text{add}}$  and  $k_{\text{dec}}$ . The excellent agreement between experiment and theory strongly indicates that not only tunneling effect but also the stabilization of the HNNO<sup>†</sup> (DNNO<sup>†</sup>) intermediate have significant contributions to the overall rate coefficient. At low temperatures ( $T < 700$  K), the contribution from the H(D) + N<sub>2</sub>O addition process becomes significant; in this process, H (or to a lesser extent D) atoms may tunnel through the barrier in step (a) and form a stable intermediate, HNNO (or DNNO) by collisional stabilization. Thus, the influence of pressure on the addition-stabilization process is also important vis-à-vis the overall tunneling effects on the total rate coefficient. The effect of pressure has also been qualitatively reported by Bozzelli et al.<sup>24</sup> through a

**TABLE 2: Calculated Rate Coefficients for Addition and Decomposition Channels of H + N<sub>2</sub>O Reaction with Ar as Buffer Gas<sup>a-c</sup>**

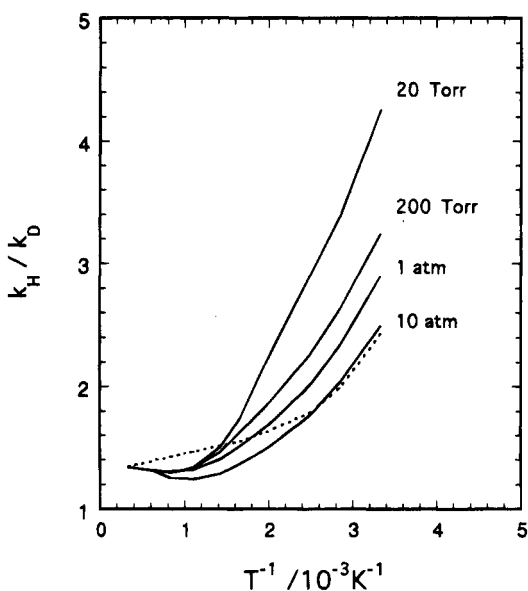
T	20		200		760		7600		∞
	add	dec	add	dec	add	dec	add	dec	add
300	5.55(-18)	7.89(-19)	1.08(-17)	3.76(-19)	1.48(-17)	2.30(-19)	2.24(-17)	8.92(-20)	2.94(-17)
500	9.36(-17)	1.67(-16)	3.75(-16)	1.50(-16)	7.58(-16)	1.39(-16)	2.46(-15)	1.14(-16)	1.01(-14)
1000	2.02(-16)	8.43(-14)	1.50(-15)	8.43(-14)	4.53(-15)	8.42(-14)	2.82(-14)	8.39(-14)	1.68(-12)
1500	9.96(-17)	1.11(-12)	8.98(-16)	1.11(-12)	3.05(-15)	1.11(-12)	2.39(-14)	1.11(-12)	1.13(-11)
2000	4.48(-17)	4.48(-12)	4.44(-16)	4.48(-12)	1.60(-15)	4.48(-12)	1.38(-14)	4.48(-12)	3.18(-11)
3000	1.08(-17)	2.00(-11)	1.18(-16)	2.00(-11)	4.49(-16)	2.00(-11)	4.31(-15)	2.00(-11)	1.01(-10)

<sup>a</sup> Rate coefficients are in units of cm<sup>3</sup> s<sup>-1</sup>, pressures in Torr, and temperatures in kelvin. <sup>b</sup> The values in parentheses represent powers of 10. <sup>c</sup> Channels add and dec represent the reaction of H + N<sub>2</sub>O to form HNNO and N<sub>2</sub> + OH, respectively.

**TABLE 3: Calculated Rate Coefficients for Addition and Decomposition Channels of D + N<sub>2</sub>O Reaction with Ar as Buffer Gas<sup>a-c</sup>**

T	20		200		760		7600		∞
	add	dec	add	dec	add	dec	add	dec	add
300	1.44(-18)	<i>d</i>	3.33(-18)	<i>d</i>	5.07(-18)	<i>d</i>	8.78(-18)	<i>d</i>	1.21(-17)
500	5.07(-17)	6.60(-17)	2.18(-16)	6.46(-17)	4.86(-16)	6.32(-17)	1.66(-15)	5.83(-17)	6.20(-15)
1000	1.67(-16)	6.41(-14)	1.26(-15)	6.41(-14)	3.69(-15)	6.41(-14)	2.58(-14)	6.40(-14)	1.16(-12)
1500	1.25(-16)	8.52(-13)	1.06(-15)	8.52(-13)	3.61(-15)	8.52(-13)	2.86(-14)	8.52(-13)	8.08(-12)
2000	1.15(-16)	3.39(-12)	1.05(-15)	3.39(-12)	3.70(-15)	3.39(-12)	3.04(-14)	3.39(-12)	2.33(-11)
3000	2.98(-17)	1.50(-11)	2.95(-16)	1.50(-11)	1.10(-15)	1.50(-11)	1.01(-14)	1.50(-11)	7.54(-11)

<sup>a</sup> Rate coefficients are in units of cm<sup>3</sup> s<sup>-1</sup>, pressures in Torr, and temperatures in kelvin. <sup>b</sup> The values in parentheses represent powers of 10. <sup>c</sup> Channels add and dec represent the reaction of D + N<sub>2</sub>O to form DNNO and N<sub>2</sub> + OD, respectively. <sup>d</sup> Negligible values.



**Figure 5.** Plot of isotope effect at various pressures as indicated. The result of high-pressure limit (corresponding to the addition/stabilization process forming HNNO) is shown as a dotted curve.  $k_H$  and  $k_D$  are the total rate coefficients for H + N<sub>2</sub>O and D + N<sub>2</sub>O, respectively.

calculation with the quantum Rice–Ramsperger–Kassel (QRRK) method, without tunneling corrections.

According to the experimental results of Marshall et al.,<sup>6,7</sup> no pressure dependence was observed with the pressure varied typically by a factor of 4 (~100–400 Torr for  $T < 700$  K). Hence contribution from both addition channels was ruled out from their qualitative QRRK<sup>6</sup> or RRKM<sup>7</sup> calculations. A search of the literature indicates that no attempt has been made to calculate the reaction rates by incorporating tunneling corrections for channel (a) in both systems. If we check the magnitude of  $\nu^*$  of channel (a) for both H + N<sub>2</sub>O and D + N<sub>2</sub>O reactions from Table 1, the noticeably high values (1287i cm<sup>-1</sup> for HNNO<sup>‡</sup>; 999i cm<sup>-1</sup> for DNNO<sup>‡</sup>) imply a necessity for tunneling corrections.

The pressure effects are shown in Figure 3A,B, which summarize the calculated total reaction rate coefficients at

various pressures for H + N<sub>2</sub>O and D + N<sub>2</sub>O, respectively. Since the addition/stabilization channels are dominant at low temperatures, they give rise to an evident pressure effect for both reactions. At high temperatures, the decomposition channels become dominant and diminish the pressure dependence. The higher the pressure is, the more important the addition channels are. At the high-pressure limit, the total rate coefficients are determined exclusively by addition channels for both reactions, shown as solid curves in Figure 3A,B.

Figure 4A,B show the temperature dependence of the rate coefficient ratio with and without tunneling corrections calculated at various pressures for H + N<sub>2</sub>O and D + N<sub>2</sub>O, respectively. The tunneling effects are significant in both H(D) reactions, especially under low-temperature and low-pressure conditions. Without tunneling corrections, the addition reaction is approximately in the third-order range at low temperatures for both reactions. But when the tunneling effect was included, the enormous enhancement in the calculated rate coefficients at low pressures changed the reaction order to the intermediate range between second and third order. Our results also show that the tunneling corrections become more essential when the pressure is lower; this will cancel part of the pressure effect and make the rate coefficients less pressure dependent. This is the reason why the H + N<sub>2</sub>O reaction has somewhat less pronounced pressure effect than D + N<sub>2</sub>O, as shown in Figure 3A,B. No such intricate  $P$  effect was observed experimentally<sup>6,7</sup> because of the narrow pressure range employed.

The overall kinetic isotope effect can also be examined in terms of the  $k_H/k_D$  ratio, plotted in Figure 5 as a function of pressure and temperature. The values of the ratio are highly pressure and temperature dependent, due primarily to the effect of tunneling as also revealed by the results presented in Figure 4. At lower pressures,  $P < 10$  atm, tunneling through both barriers are important, whereas at higher pressures, when all of the excited adducts (HNNO<sup>‡</sup> or DNNO<sup>‡</sup>) are collisionally deactivated, only the effect of tunneling through the first barrier affects the  $k_H/k_D$  ratio, as indicated by the dotted curve in Figure 5.

The selected RRKM results of H + N<sub>2</sub>O and D + N<sub>2</sub>O for both addition and decomposition channels are tabulated in Table

2 and 3, respectively, for  $P(\text{Ar})/\text{Torr} = 20, 200, 760, 7600,$  and  $\infty$  at six temperatures between 300 and 3000 K. For the convenience of kinetic modeling, we provide the analytical equations obtained from the least-squares fitting of our results at 760 Torr for the temperature range of 300–3000 K:

$$k_{\text{H}} = 2.58 \times 10^{-26} T^{4.39} e^{-1455/T}$$

$$k_{\text{D}} = 4.40 \times 10^{-25} T^{4.01} e^{-1980/T}$$

both expressed in units of  $\text{cm}^3 \text{s}^{-1}$ .

### Conclusions

The rate coefficients for the  $\text{H}(\text{D}) + \text{N}_2\text{O}$  reactions, including both addition and decomposition channels, have been calculated over a wide range of conditions with the numerical solution of master equations<sup>15</sup> based on the RRKM theory with tunneling corrections using the thermochemical data computed by the BAC-MP4 method. The generalized Eckart potential was introduced to calculate the one-dimensional tunneling probability along the reaction coordinate.<sup>19–22</sup> The calculated results agree with the experimental data of Marshall et al.<sup>7</sup> over the temperature range 400–1300 K.

At low temperatures ( $T < 700$  K), the reactions are dominated by the pressure-dependent addition–stabilization process with noticeable tunneling effect through barrier (a) to produce the stable intermediate (HNNO or DNNO). However, our results show that the tunneling effect makes the rate coefficients less pressure dependent, which explains the difficulty in observing the effect of pressure experimentally. At temperatures  $> 700$  K, the decomposition channel becomes dominant, while the formation of HNNO(DNNO) by collisional deactivation as well as the effect of tunneling through barrier (b) diminish rapidly with increasing temperature. The overall kinetic isotope effect has also been examined by the ratio of  $k_{\text{H}}/k_{\text{D}}$ , which exhibits strong  $P/T$  dependencies, due to the effects of collisional deactivation and quantum-mechanical tunneling.

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### References and Notes

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