Thermal Decomposition of HN₃

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The two-channel thermal decomposition of hydrogen azide, HN₃, was studied computationally. The reaction produces triplet or singlet NH and N₂. A model of the reaction was created on the basis of the theoretical study of the reaction potential-energy surface and microscopic reaction rates by Besora and Harvey (Besora, M.; Harvey, J. N. *J. Chem. Phys.* **2008**, *129*, 044303) and the experimental data on the energy-dependent rate constants reported by Foy et al. (Foy, B. R.; Casassa, M. P.; Stephenson, J. C.; King, D. S. *J. Chem. Phys.* **1990**, *92*, 2782) The properties of the model were adjusted to fit the calculated k(E) dependence to the experimental one. The experiments on thermal decomposition of HN₃ described in the literature were analyzed via kinetic modeling; the results of the analysis demonstrate that all but one of the existing studies were affected by contributions from secondary kinetics. The model of the reaction was then used in master-equation calculations of the pressure effects and the value of the critical energy transfer parameter, ΔE_{down} , was adjusted based on agreement with the experimental k(T,P) data. Finally, the model was used to determine pressure and temperature-dependent rate constants for both channels of reaction 1, which do not conform to the traditional formalism of low-pressure-limit and falloff description. Uncertainties of the model and their influence on the calculated thermal rate constant values were analyzed. Finally, parametrized expression for rate coefficients were provided for a wide range of temperatures and pressures.

I. Introduction

Hydrogen azide, or hydrazoic acid (HN₃), is an explosive liquid with high energy density. It is known to thermally decompose in a slow or explosive way.¹ It is a product of the first elementary reaction step in the pyrolysis of 5-aminotetrazole, CH_3N_5 ,^{2,3} which is widely used as a gas generator and as an ingredient in solid rocket propellants.^{4–7} Understanding and control of combustion and pyrolysis of 5-aminotetrazole requires knowledge of the mechanism and kinetics of thermal decomposition of HN₃.

The initiation reaction of the pyrolysis or combustion of HN_3 is the elementary reaction of its thermal dissociation. Two channels are possible: the spin-forbidden pathway forming triplet ³NH and N₂ and the spin-allowed channel resulting in formation of singlet ¹NH and N₂:

$$HN_3 \rightarrow {}^{3}NH + N_2 \quad \Delta H_{298}^{\circ} = 7.5 \text{ kcal mol}^{-1} \quad (1a)$$

$$\rightarrow {}^{1}\mathrm{NH} + \mathrm{N}_{2} \quad \Delta H^{\circ}_{298} = 45.7 \text{ kcal mol}^{-1}$$
(1b)

Here, the values of ΔH°_{298} are based on quantum chemical calculations of Besora and Harvey,⁸ which also indicate that the energy barrier for the less endothermic spin-forbidden pathway is lower than that for the spin-allowed channel 1b (below).

HN₃ decomposition has been studied experimentally by four groups; all of these studies have been performed in shock tubes

with argon as the bath gas. Zaslonko et al.⁹ used 1.0-2.1% HN₃/ Ar mixtures with small added amounts of CO₂. These authors determined the rates of HN₃ decomposition by monitoring IR emission at 4.67 μ m in real time and using the initial slopes of the kinetic curves. Kajimoto et al.¹⁰ used somewhat lower concentrations of HN₃ in argon (0.07-0.33%) and monitored HN₃ decay by UV absorption spectroscopy at 206 nm. Logarithmic plots of HN₃ decays were linear within the first 100 μ s; the slopes of the respective plots were used to determine the rate constants. Dupré et al.11 studied reaction 1 using IR and UV emission spectroscopy and HN₃/Ar mixtures with 0.5% and 2.0% concentrations. The rate constants were evaluated from half-times of the 4.67 μ m HN₃ emission signal. These authors observed differences between the rate constant values obtained using the lower and the higher HN₃ concentrations, with higher HN₃ concentrations resulting in faster decays. Finally, Röhrig and Wagner¹² determined the rate constants of HN₃ decomposition using UV absorption spectrometry as a means of detecting the ³NH product. These authors used significantly lower concentrations of HN₃ compared to those of the earlier studies, 9^{-11} in the 1–30 ppm range. As will be shown below, using such low concentrations enabled direct determination of k_1 in ref 12, whereas the results of the earlier studies have to be corrected for the influence of secondary reactions.

In addition to thermal studies of reaction 1,^{9–12} which provide temperature-dependent rates of decomposition, two vibrational overtone spectroscopy investigations by Foy et al.^{13,14} resulted in determination of energy-dependent rate constants of reaction 1 in the 181–211 kJ mol⁻¹ range. Finally, reaction 1 was studied theoretically by a number of authors.^{8,15–17} The recent work of Besora and Harvey⁸ refined the details of the potential-energy surface (PES) of both channels by using accurate electronic structure methods and calculated energy-dependent k(E) func-

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Figure 1. Temperature dependences of the rate constants of reaction 1 reported in experimental studies of Röhrig and Wagner,¹² Kajimoto et al.,¹⁰ Zaslonko et al.,⁹ and Dupre et al.¹¹

tions using a nonadiabatic version of the RRKM method. Their analysis included details of PES in the vicinity of the minimum energy crossing point between the singlet and the triplet potential-energy surfaces; the energy-dependent probability of singlet—triplet transition was calculated using a semiclassical method^{18–20} that includes the effects of tunneling, which were shown to be substantial for the reaction channel 1a. The results of the k(E) calculations of Besora and Harvey are in approximate agreement with the experimental data of Foy et al., with two limiting calculated k(E) dependences corresponding to different treatments of the overall molecular rotations bracketing the experimental data.

The main purpose of the current work is to study the temperature- and pressure-dependent thermal kinetics of reaction 1 by using the existing theoretical and experimental information on its mechanism and microscopic energy-dependent rates. Here, a model of reaction 1 was created on the basis of the theoretical study of Besora and Harvey⁸ and the experimental data of Foy et al.;^{13,14} the calculated k(E) dependence was adjusted to fit the experimental one. The experiments on thermal decomposition of HN₃ described in the literature⁹⁻¹² were analyzed via kinetic modeling. The model of reaction 1 was then used in master-equation calculations of the pressure effects and the value of the critical energy transfer parameter, ΔE_{down} , was adjusted based on agreement with the experimental k(T,P) data. Finally, the model was used to determine pressure- and temperaturedependent rate constants for both channels of reaction 1, which do not conform to the traditional formalism of low-pressurelimit and falloff description. Uncertainties of the model and their influence on the calculated thermal rate constant values were analyzed. Finally, parametrized expression for rate coefficients are provided for a wide range of temperatures and pressures.

The article is organized as follows. This section is an introduction. Section II describes the existing experimental data on thermal and energy-dependent reaction and the kinetic analysis of the thermal data. Section III describes the computational model development. Section IV presents the results and the discussion.

II. Experimental Data on Thermal and Energy-Dependent Dissociation of HN_3

Thermal Dissociation. As described in the Introduction, all experimental studies of reaction 1 have been performed in shock tubes with spectroscopic detection of the HN_3 reactant or/and the NH products.^{9–12} The results of these investigations, expressed by their respective authors as second-order rate constants, are presented in Figure 1 in Arrhenius coordinates. In some of these studies, relatively high concentrations of HN_3

were used, which resulted in the formation of correspondingly high concentrations of the NH products. As will be shown below, subsequent secondary reactions occurred on the time scales comparable with the time scales of the primary reaction, which interfered with the determination of the rate constants of reaction 1. Kajimoto et al.¹⁰ analyzed the kinetics of secondary reactions occurring under the conditions of their experiments using a mechanism consisting of 10 reactions. These authors concluded that the singlet ¹NH biradicals produced in the reaction channel 1b will very rapidly react with HN₃, thus doubling the observed rate of HN₃ disappearance due to reaction 1b. However, the fraction of the singlet pathway was concluded to be minor by the authors of ref 10 and, based on the results of their kinetic modeling, they chose not to modify the observed rates of reaction 1.

The kinetic mechanism used in the current work (Table 1) is based on that of Kajimoto et al.¹⁰ However, the rate constants of the constituent reactions are, generally, different. These rate constants were selected on the basis of experimental or computational studies,^{21–26} as described below. In each run of numerical kinetics simulations, conditions were selected to match those of a particular experimental study. The rate of reaction 1 was selected to achieve a match between the experimentally observed rate of HN₃ decay and that resulting from modeling. The ³NH and ¹NH biradicals produced in reaction 1 can react with HN₃:

$$^{3}NH + HN_{3} \rightarrow NH_{2} + N_{3}$$
 (2a)

$${}^{1}\mathrm{NH} + \mathrm{HN}_{3} \rightarrow \mathrm{NH}_{2} + \mathrm{N}_{3}$$
(2b)

Reaction 2b is fast, with the rate constant close to the collision rate, with the preexponential factor of $8.1 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1}$ s⁻¹ and a very small activation energy of 0.76 kJ mol^{-1,27} Under the conditions of three $^{9-11}$ of the four experimental studies of reaction 1, high concentrations of HN3 (2.3 \times 10⁻⁹ to 8.0 \times 10^{-7} mol cm⁻³) resulted in almost instantaneous, on the experimental time scale, consumption of the second HN₃ molecule. However, as will be shown below, channel 2b is minor under the conditions of most experiments. Thus, kinetic modeling was performed with only the reaction channel 2a included in the mechanism. The temperature dependence of k_{2a} was taken from the theoretical study of Henon and Bohr,²¹ who performed high-level electronic structure calculations on a series of reactions (including reactions 2 and 5) and obtained rate constant values in transition-state theory calculations with tunneling correction. The authors of ref 21 did not provide analytical expressions for the rate constants and the expression given in Table 1 was obtained here by fitting the data of Henon and Bohr in the 800-2000 K temperature range.

The rate constant of reaction 3 was determined in shock tube experiments of Mertens et al.²² in the 2070–2730 K range. Following the arguments of Kajimoto et al., we assign the 2H + N₂ products to this reaction. Rate constants recommended in a review by Baulch et al.²³ were used for reactions 4 and 9. Reaction 5 was studied in direct discharge flow–mass spectrometry experiments by Le Bras and Combourieu²⁴ in the 300–460 K temperature range. A later theoretical work of Henon and Bohr²¹ yielded rate constants in agreement with those of the experimental study of ref 24. In their modeling, Kajimoto et al. modified the Arrhenius parameters of ref 24 to achieve better agreement with their experimental HN₃ profiles; this modification reduced the rate constants by a factor of ~26 in

TABLE 1: Rate Constants Used in the Kinetic Simulation of HN₃ Decomposition

reaction number	reaction	A^a	п	$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$	ref
1	$HN_3 \rightarrow {}^3NH + N_2$				exptl ^b
2a	$^{3}NH + HN_{3} \rightarrow NH_{2} + N_{3}$	7.83×10^{2}	3.19	41.7	21
3	$^{3}NH + ^{3}NH \rightarrow H + H + N_{2}$	5.13×10^{13}	0	0	22
4	$^{3}NH + H \rightarrow H_{2} + N$	1.02×10^{13}	0	0	23
5	$H + HN_3 \rightarrow NH_2 + N_2$	1.53×10^{13}	0	19.3	24
6	$NH_2 + HN_3 \rightarrow NH_3 + N_3$	6.00×10^{11}	0	4.6	10
7	$NH_2 + NH_2 + M \rightarrow N_2H_4 + M$	1.00×10^{18}	0	0	25
8	$H + NH_2 + M \rightarrow NH_3 + M$	2.20×10^{18}	0	0	26
9	$H + H + M \rightarrow H_2 + M$	2.19×10^{15}	-1.00	0	23
10	$N_3 + HN_3 \rightarrow 3 N_2 + H$	1.00×10^{11}	0	0	estimated ^c

^{*a*} The units are mol, cm³, and s. ^{*b*} Each value was selected to achieve a match between the modeled rate of HN₃ decay and that observed in a particular experiment. ^{*c*} This rate constant was varied by a factor of 100 (text).

the 1201-1347 K experimental temperature range of ref 10 relative to the values resulting from the original expression.²⁴ Extrapolation of low-temperature data to higher temperatures is associated with uncertainty; however, one can generally expect the rate constants at high temperatures to be somewhat higher than suggested by the low-temperature Arrhenius extrapolation because of the typical positive curvatures of Arrhenius plots for bimolecular reactions with energy barriers. In that respect, the adjustment of the rate constant undertaken by Kajimoto et al. is probably unrealistic. In the modeling performed in the current work, the original expression of Le Bras and Combourieu²⁴ is used. For reaction 6, no experimental or theoretical data are available; thus, the BEBO estimate of Kajimoto et al. is used. The experimental third-order rate constant of Khe et al.²⁵ is used for the recombination of NH_2 (reaction 7) in Ar bath gas; the experimental rate constant value of Gordon et al.²⁶ is used for reaction 8. There are no experimental or theoretical studies of reaction 10, that of N₃ with HN₃. N₃ is known to react rather efficiently with NO2 (reported room temperature rate constants are 1.2×10^{12} cm³ mol⁻¹ s^{-1 28} and 5×10^{11} cm³ mol⁻¹ s^{-1 29}) and even more efficiently with NO,^{28,29} with attack on the nitrogen atom. These reactions, however, are not good analogies because NO and NO2 are open-shell species, whereas HN_3 is not. Here, we use a conservative estimate of 1×10^{11} $\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the rate constant of this reaction at T > 1200K and the effects of increasing this value by 2 orders of magnitude on the kinetic modeling are investigated.

Below, the results of analysis of the existing experimental studies of reaction 1 using the kinetic mechanism of Table 1 are presented. Kinetic modeling was performed using the IBM Chemical Kinetics Simulator.³⁰ This modeling is used in qualitative or semiquantitative way, to evaluate the approximate correction factors that need to be applied to the reported rate constants and to determine which of the experimental studies, if any, can be used as a basis for the computational model of reaction 1.

The most recent investigation of reaction 1 is that of Röhrig and Wagner.¹² The relative concentrations of HN₃ used were in the 0.9–3 ppm range, with the total gas pressure of 227–297 Torr at 1398–1779 K, which translates into the $(2.3-7.8) \times 10^{-12}$ mol cm⁻³ range of the absolute concentrations. Such low concentrations of HN₃ and, consequently, of the products of decomposition make secondary reactions negligible under the conditions of these experiments; the reported rate constants require no corrections. ³NH was observed as the major product of reaction 1 and any potential contribution of channel 1b producing the ¹NH biradical was ruled to be negligible.

The study of Kajimoto et al.¹⁰ was performed in the 1201–1347 K temperature range and pressures between 606

and 2187 Torr. The concentrations of HN_3 was in the (1.1–2.6) \times 10⁻⁸ mol cm⁻³ range. The rate constants were determined from the slopes of the logarithmic plots of the HN₃ signal as a function of time within the first 100 μ s of decay. Formation of ³NH in reaction 1 and its slower subsequent decay were also observed. Modeling of the secondary kinetics under the conditions of these experiments was performed in the current work using the mechanism of Table 1 and the effective first-order rates of HN₃ decay were obtained using the procedure of ref 10, that is, by fitting the first 100 μ s of the ln([NH₃]) versus time dependences. The correction factors obtained by dividing the effective decay rates by the first-order rate constants of reaction 1 used in the kinetic mechanism ranged from 1.40 to 1.73, with the average value of 1.57. Effects of variations of the rate constants of reactions 2-10 within a factor of 2 on the correction factor were investigated. The effects were in the range of 0-10% of the calculated correction factors, with the largest effect caused by the changes in the rate constant of reaction 5. Increasing the rate constant of reaction 10 by a factor of 100 had a relatively minor effect (8%).

The work of Zaslonko et al. involved the concentrations of HN₃ in the $(2.5-8.0) \times 10^{-8}$ mol cm⁻³ range at T = 1255-1615K and the pressures of 2.3-8.4 atm. The rate constants of reaction 1 were determined from the initial slopes of the HN₃ signal decay curves. In the text of the article, species profiles obtained under conditions where the characteristic HN₃ decay time is $\sim 30 \ \mu s$ are referred to as not being sufficiently clear and resolved; nevertheless, the main data table includes k_1 values as high as 5.9×10^5 s⁻¹, corresponding to the reaction halftime of 1.2 μ s. The kinetic analysis performed in the current work included only the data from experiments with $k_1 \leq 1 \times 1$ 10^5 s^{-1} because those where higher values of k_1 were obtained could have suffered from insufficient temporal resolution. The correction factor obtained in the analysis is in the 1.52-2.34 range, with the average value of 1.83. It should be noted that scattering of the individual data points is comparable in magnitude to the secondary kinetics correction factors.

Dupre et al.¹¹ performed their experiments on the kinetics of reaction 1 at the pressures in the 55–200 Torr range and the temperatures between 1150 and 2000 K. Rate constant values were obtained from the measurements of HN₃ half-life times. Two values of the relative concentration of HN₃ were used, 0.5% and 2.0%, with the experiments performed using the lower HN₃ concentration yielding lower values of the rate constant. The temperature dependences obtained below and above 1450 K are characterized by different activation energies (116 and 81 kJ mol⁻¹, respectively). The conditions and the results of individual experiments are not reported but two Arrhenius expressions are given for the results of the low HN₃ concentration experiments,



Figure 2. Energy-dependent rate constants of the two channels of reaction 1. Symbols represent the experimental data by Foy et al.^{13,14} Solid and dashed lines represent the central and the limiting models, respectively (text). Energy barriers are shown by the dotted lines.

for the 1250-1400 K and the 1450-1720 ranges. However, the values of the rate constants between 1250 and 1400 K presented in figure 6 of ref 11 are lower than those suggested by the Arrhenius expression given for this temperature range by an average factor of 1.8. The source of the inconsistency is unclear. Kinetic modeling was performed for the experiments of Dupre et al. using the limiting values of the overall pressure and 0.5% concentration of HN₃. The resultant secondary kinetics correction factors are in the 1.28-2.30 range, with the average value of 1.65.

The results of kinetic modeling demonstrate that only the experiments of Röhrig and Wagner¹² were free of any complications from secondary reactions. These $k_1(T)$ data were thus used as a basis for creating a computational model of reaction 1. Predictions of this model were compared with the results of Kajimoto et al.¹⁰ corrected for the secondary kinetics (below). The results of Zaslonko et al.⁹ and Dupre et al.¹¹ were not used in such comparison. The study of ref 11 suffered from significant uncertainties in the description of the results, as described above. The results of Zaslonko et al. are in general approximate agreement with those of Röhrig and Wagner and Kajimoto et al., as can be seen from the plot in Figure 1. However, large data scattering and concerns about temporal resolution (above) make any further comparison rather meaningless.

Energy-Dependent Rate Constants. Foy et al.^{13,14} studied reaction 1 by the method of vibrational overtone dissociation. HN₃ molecules were vibrationally excited to energies corresponding to multiple vibrational quanta by a laser pulse and appearance of the ³NH product was monitored by laser induced fluorescence. The energy-dependent dissociation lifetimes were measured by varying the time delay between the pump and the probe laser pulses and thus monitoring the ³NH signal as a function of time; exponential rising profiles were obtained. In ref 13, two values of the dissociation lifetimes were obtained in free-jet expansion experimental setup, with the effective temperature of 8 K; in ref 14 both the free jet expansion and a gas cell kept at 300 K were used, with similar results. The results of these studies expressed as dissociation rate constants are presented in Figure 2 as a function of vibrational energy. It should be noted that, although the product of the reaction channel 1a was monitored, the energy-dependent rate constants were determined from the dissociation lifetimes and thus represent the overall reaction, with potential contribution from the reaction channel 1b as well, if such a contribution is present.

III. Computational Model of Reaction 1

Energy-Dependent Rate Constants. The model developed in the current work is based on the recent theoretical study of

Besora and Harvey.^{8,31} These authors studied the potentialenergy surfaces (PES) and the energy-dependent kinetics of the two channels of reaction 1 using high-level electronic structure methods and the RRKM theory.^{32–35} For the reaction channel 1a involving a singlet-triplet transition, nonadiabatic RRKM methods¹⁸ were used, adapted by Harvey et al.^{19,20} for efficient use of the calculated properties of the PES in the vicinity of the minimum energy crossing point between electronic potential-energy surfaces. The reaction PES was studied using several quantum chemical methods; energy-dependent rate constants were calculated using the CASSCF/cc-pVTZ-based rotational constants and vibrational frequencies and the MR-AQCC/cc-pVTZ³⁶⁻³⁸ level energies; the properties of the crossing point between the potential-energy surfaces were obtained using a hybrid method involving reoptimization that used CASSCF/cc-pVTZ energy gradients but MR-AQCC/ccpVTZ level energies.

Besora and Harvey calculated energy-dependent rate constants for the reaction channels 1a using three models. One model used Landau-Zener expression for singlet-triplet transition probability, which does not account for tunneling. The second and the third models included semiclassical approximation for tunneling, which resulted in significantly different shapes of the $k_{1a}(E)$ dependences, where instead of a sharp cutoff at the energy equal to the barrier height the $k_{1a}(E)$ function falls off more slowly at energies below the barrier. These models differed in their treatment of the overall rotations of the HN₃ molecule and the transition state. One model treated the overall rotations as active, that is, capable of freely exchanging energy with the vibrational degrees of freedom, and the other treated them as inactive or adiabatic (refs 32-35 for discussions of active and adiabatic degrees of freedom). Comparison of the results of the calculations with those of the experiments of Foy et al.^{13,14} showed that the two calculated $k_{1a}(E)$ dependences obtained with the models that included tunneling bracketed the experimental data, with the all-active and the all-adiabatic models giving $k_{1a}(E)$ values that are below and above the experimental data, respectively. The rate constants of channel 1b were calculated using the RRKM method with all rotational degrees of freedom treated as active.

In the current work, the $k_{1a}(E)$ dependence of Besora and Harvey (numerical array obtained from the authors³¹) was used as the initial approximation. Then the model was adjusted to include the most conventional treatment of the rotational degrees of freedom, where the molecule is approximated with a symmetric top, and the overall 2D rotation with a large moment of inertia is treated as adiabatic, whereas the 1D rotation with a small moment of inertia is treated as active.^{32–35} The critical energy of the intersurface crossing point was adjusted to obtain the best fit between the calculated and the experimental k(E)dependences. Details of this process are described below.

The RRKM expression for the energy-dependent rate constant is given by the equation

$$k(E) = \frac{N(E)}{h\rho(E)} \tag{I}$$

Here, N(E) and $\rho(E)$ are the sum-of-states and the densityof-states functions of the transition state and the reactive molecule respectively, and *h* is the Planck's constant. For a reaction where tunneling and/or nonadiabatic transitions are possible, a similar expression having the same form is used, except that the N(E) function is substituted with a modified $N_{\rm T}(E)$ function, which is obtained by a convolution of the transition-state density of states with the energy-dependent reaction probability function.^{8,18–20,39,40}

$$k(E) = \frac{N_{\rm T}(E)}{h\rho(E)} \tag{II}$$

The differences caused by inclusion or exclusion of the 1D active rotational degree of freedom influences the k(E) function through the densities of states of the reactant molecule and the transition state. In principle, it is possible to obtain numerical values of the $N_{\rm T}(E)$ function with the density-of-states function of the 1D rotor included through a numerical convolution procedure. However, given the finite energy step of the available k(E) numerical array, a different method was used here. First, an RRKM model of reaction channel 1a was created with a pseudo transition state and all rotational degrees of freedom treated adiabatically. This model included a possibility of tunneling (with the effective barrier width parameter^{41,42} of 2.4) and an artificial transmission probability factor of 0.025. The properties of the transition state were modified to fit the resultant log ($k_{1a}(E)$) dependence to the numerical array obtained³¹ from the authors of ref 8; the resultant rms deviation was 0.08. Second, the model was modified to include one active 1D overall rotation in both the HN₃ molecule and the transition state. Third, the $k_{1a}(E)$ values obtained from Besora and Harvey were scaled by the ratio of the rate constants obtained in steps 2 and 1. This procedure provided an approximation to the $k_{1a}(E)$ function obtained using the theoretical method of Besora and Harvey but with one overall rotational degree of freedom treated as active.

In the final, fourth step, the $k_{1a}(E)$ array was modified by adjusting the energy of the minimum energy crossing point to obtain the best fit of the experimental dependence of k_{1a} on energy (Figure 2) at energies below 210 kJ mol⁻¹. In this process, the $N_T(E)$ array was shifted along the energy scale until optimum agreement between the experimental and the calculated $k_{1a}(E)$ dependences was achieved, which corresponded to a 3.6 kJ mol⁻¹ downward shift. All calculations of the energydependent rate constants and the $\rho(E)$ density of states function needed for such calculations were performed using the *Chem-Rate* program.⁴³

The energy dependence of the microscopic rate constant for the singlet channel, $k_{1b}(E)$, was calculated using the RRKM method and assuming one active 1D rotational degree of freedom. The molecular structure and the vibrational frequencies of the transition state was obtained from Besora and Harvey.^{8,31} The energy of the corresponding transition state was slightly adjusted (by 1.55 kJ mol⁻¹) relative to the value obtained by Besora and Harvey in the MR-AQCC/cc-pVTZ calculations by fitting the resultant $k_{1b}(E)$ dependence so that it passes through the highest-energy experimental data point in Figure 2. This data point is located outside the estimated envelope of uncertainties for the $k_{1a}(E)$ dependence; thus, adjustment of the energy barrier for the singlet channel was based on the expectation that the major contribution to the overall rate constant at this energy comes from the $k_{1b}(E)$ function.

In addition to the model of reaction 1 described above, which is referred to henceforth as the central model, four limiting models were also created to investigate the effects of reasonable variation in the model properties on the k(E) dependences and the corresponding thermal rate coefficients. The envelope of uncertainties for the $k_{1a}(E)$ dependence (shown by the dashed lines in Figure 2) was determined by the scatter of the experimental data points on the plot. Two of the limiting models correspond to the \pm 3.6 kJ mol⁻¹ shifting of the minimum energy crossing point on the energy scale. Two more limiting models were created by upward and the downward shifting of the energy of the transition state of the reaction channel 1b. The uncertainties in the $k_{1b}(E)$ dependence can be roughly evaluated based on the uncertainty in the energy barrier for the singlet channel, which was estimated at 2 kcal mol⁻¹ (8.4 kJ mol⁻¹). Thus, the upper limit for the energy barrier was obtained by adding 8.4 kJ mol⁻¹ to the value used in the central model. At the same time, subtracting 8.4 kJ mol⁻¹ from the central value of the energy barrier would result in complete disagreement with the experimental k(E) data (Figure 2) as it would yield the overall k(E) value well above 10^{10} s⁻¹ at the highest energy of the experimental range, 211 kJ mol⁻¹, more than an order of magnitude above the experimental value. Thus, the lower limit of the energy barrier for the reaction channel 1b was obtained by subtracting only 2 kJ mol⁻¹ from the value used in the central model. The resultant upper-limit $k_{1b}(E)$ dependence (the upper dashed line on the $k_{1b}(E)$ plot in Figure 2) still passes noticeably higher than the experimental data point at 211 kJ mol⁻¹ but the difference is comparable with the average reported experimental uncertainty in k(E) and the scatter of the experimental data.

Thermal Rate Constant Calculations. Pressure- and temperature-dependent rate constants of HN₃ decomposition were calculated via solution of a steady-state master equation³⁴ using the Nesbet algorithm.⁴⁴ The exponential-down^{34,45} model of collisional energy transfer was used in the calculations. It was demonstrated that the calculated rate constant values did not depend on the size of the energy increment (50 cm⁻¹ used in the master-equation solution with 5 cm⁻¹ used in *k*(*E*) calculations) used in converting the continuous form of the master equation into the matrix form.³⁴ The *ChemRate* program⁴³ was used in all calculations.

IV. Results and Discussion

The values of the collisional energy transfer parameter, $\langle \Delta E \rangle_{\text{down}}$ (average energy transferred per deactivating collision with the bath gas), is unknown and can only be obtained from fitting of the experimental data. This parameter, generally, has an unknown temperature dependence. Two models of the $\langle \Delta E \rangle_{\text{down}}$ versus temperature dependence for HN₃ were used in the current study. The first model employed a temperatureindependent $\langle \Delta E \rangle_{\text{down}} = \text{constant}$ and the second model used a proportional $\langle \Delta E \rangle_{\text{down}} = \alpha T$ dependence (by analogy with earlier studies of decomposition of small polyatomic molecules, for example, refs 46–48). The values of $\langle \Delta E \rangle_{\text{down}}$ (for the $\langle \Delta E \rangle_{\text{down}}$ = constant model) and coefficient α (for the $\langle \Delta E \rangle_{down} = \alpha T$ model) for the collisions between HN₃ and argon bath gas were adjusted to achieve agreement with the experimental rate constants of Röhrig and Wagner.¹² The resultant values are $\langle \Delta E \rangle_{\rm down} = 349 \text{ cm}^{-1}$ and $\alpha = 0.217 \text{ cm}^{-1} \text{ K}^{-1}$. The use of the $\langle \Delta E \rangle_{\text{down}} = \alpha T$ model resulted in the faster then the experimental rise of the rate constants with temperature; thus, the $\langle \Delta E \rangle_{\text{down}}$ = constant model was selected for further use. To evaluate the effect of the uncertainties in the $k_{1a}(E)$ and $k_{1b}(E)$ dependences, the fitting process was repeated with the limiting models, which resulted in different $\langle \Delta E \rangle_{down}$ values. The resultant values of $\langle \Delta E \rangle_{\text{down}}$ are given in the Supporting Information.

Figure 3 shows the calculated values of the rate constants in comparison with the experimental data of refs 12 and 10. Reaction 1 is not exactly in the low-pressure limit under the conditions of these experiments (below), as is typical for reactions affected by tunneling.⁴² Thus, even though both Röhrig



Figure 3. Calculated values of the rate constants of reaction 1 in comparison with the experimental data of Röhrig and Wagner¹² and Kajimoto et al.¹⁰ The solid line represents rate constants calculated for the pressure of 255 Torr and the dashed line – those calculated for the pressure of 1200 Torr. Because the experiments of ref 10 cover a wide range of pressures and the reaction does not exactly conform to the second-order rate law, to enable a comparison, the experimental values of the rate constant reported in ref 10 were first corrected for the influence of secondary kinetics and then reduced to the same pressure (text).

and Wagner and Kajimoto et al. expressed their experimental results as second-order rate constants, comparing the calculated and the experimental data requires use of the experimental pressures in calculations. All experiments of ref 12 were performed within a narrow range of pressures, 227–297 Torr. Thus, for comparison purposes, the temperature dependence of the overall rate constant of reaction 1 calculated for the average pressure of 255.5 Torr and expressed as a second-order rate constant is presented in Figure 3. The agreement between the calculations and the experiment is good, as can be expected because of the adjustment of the $\langle \Delta E \rangle_{\text{down}}$ parameter performed in the fitting process. Comparison between the calculated and the experimental data for the conditions of the experiments of Kajimoto et al. is not as straightforward. The experiments were performed in the 606-2187 Torr pressure range, and deviations from the low-pressure-limit behavior of reaction 1 are significantly different for the upper and the lower boundaries of this pressure range. In addition, as was discussed above, secondary kinetics influenced the rates of HN₃ disappearance in these experiments, thus affecting the reported rate constant values. Thus, to enable a comparison, the experimental values of the rate constant reported in ref 10 were first corrected for the influence of secondary kinetics and then reduced to the same pressure (1200 Torr). Correction for secondary kinetics was done by dividing the reported rate constants by the correction factors determined in the kinetic modeling described in section II of the article. Reduction to the same pressure was performed by multiplying each experimental rate constant by the ratio of the calculated rate constants obtained at 1200 Torr and at the corresponding actual experimental pressure. As can be seen from the plot, the calculated rate constants are in good agreement with the corrected and reduced experimental values.

The values of k_{1a} and k_{1b} were calculated over wide temperature and pressure ranges (800–3000 K, 1–10⁵ Torr) using the central and the four limiting models of reaction 1. The highpressure-limit rate constants calculated in the same temperature range can be represented by the following Arrhenius expressions:

$$k_{1a}^{\infty} = 5.6 \times 10^{11} \exp(-22180 \text{ K/T}) \text{ s}^{-1}$$
 (III)

$$k_{1b}^{\infty} = 9.3 \times 10^{14} \exp\left(-26460 \text{ K/T}\right) \text{ s}^{-1}$$
 (IV)

The pressure dependences of the rate constants of the two channels are presented in Figure 4, parts a and b; the pressure dependence of the singlet-to-triplet ratio of the rate constants is shown in part c of Figure 4. Detailed tables of the calculated rate constants are given in the Supporting Information. As can be seen from the plots, the pressure dependences do not conform to the traditional formalism of low-pressure-limit and falloff description. For example, at low pressures the pressure dependence of the rate constant of the singlet channel is stronger than linear; under some conditions, the rate constant increases as a square of pressure. Such behavior is caused by the change in the relative importance of the two channels with pressure, illustrated by a family of S-shaped curves of the k_{1b}/k_{1a} ratios as functions of pressure in part c of Figure 4. At low pressures, the steady-state population of HN3 is severely depleted at energies above the lower of the two barriers, that for channel 1a. Thus, the lower-energy channel dominates. At high pressures, the energy distribution is closer to the Bolzmann function and the higher-energy singlet channel becomes more important because of the higher k(E) values. The falloff curves obtained for the triplet channel are extended far into the low-pressure range of the plot, not reaching the low-pressure limit even at the low pressure of 1 Torr at the highest temperature used in calculations at 3000 K. This kind of behavior is caused by the effects of tunneling on the shape of the k(E) dependence.⁴²

Because of the larger preexponential factor, the singlet channel dominates in the high-pressure limit at all temperatures used, with the $k_{1b}^{\infty}/k_{1a}^{\infty}$ ratio increasing with temperature; this



Figure 4. Calculated pressure dependences of (a, b) the rate constants of the two channels of reaction 1 and (c) the singlet-to-triplet ratio of the rate constants.

TABLE 2: Chebyshev Polynomial Coefficients $a_{i,j}^{a}$ for Falloff Parameterization

j	i = 1	i = 2	i = 3	i = 4	i = 5				
Channel 1a, Ar Bath Gas									
1	2.469	1.362	-2.828×10^{-1}	-3.374×10^{-2}	1.203×10^{-2}				
2	-3.264	-4.355×10^{-1}	6.220×10^{-3}	2.428×10^{-2}	-6.969×10^{-3}				
3	-2.922×10^{-1}	1.134×10^{-2}	9.162×10^{-3}	-7.847×10^{-4}	-3.292×10^{-5}				
4	6.074×10^{-2}	8.866×10^{-3}	-4.204×10^{-4}	-2.037×10^{-4}	2.160×10^{-4}				
5	-6.618×10^{-3}	-4.069×10^{-3}	-2.801×10^{-4}	1.062×10^{-4}	-4.939×10^{-5}				
Channel 1b, Ar Bath Gas									
1	7.336×10^{-1}	4.194	-4.932×10^{-1}	-1.977×10^{-1}	3.809×10^{-2}				
2	-3.635	-2.208×10^{-1}	-1.422×10^{-1}	1.932×10^{-2}	-1.376×10^{-2}				
3	-3.270×10^{-1}	-6.725×10^{-3}	1.311×10^{-2}	1.110×10^{-4}	-2.151×10^{-4}				
4	6.461×10^{-2}	9.019×10^{-3}	-1.882×10^{-3}	-3.831×10^{-4}	2.739×10^{-4}				
5	-7.681×10^{-3}	-4.195×10^{-3}	1.053×10^{-4}	2.087×10^{-4}	-7.657×10^{-5}				
Channel 1a, N ₂ Bath Gas									
1	2.516	1.328	-2.866×10^{-1}	-2.719×10^{-2}	1.046×10^{-2}				
2	-3.277	-4.355×10^{-1}	9.448×10^{-3}	2.399×10^{-2}	-7.554×10^{-3}				
3	-2.917×10^{-1}	1.205×10^{-2}	9.056×10^{-3}	-1.080×10^{-3}	2.298×10^{-4}				
4	6.103×10^{-2}	8.875×10^{-3}	-4.070×10^{-4}	-1.368×10^{-4}	1.915×10^{-4}				
5	-6.781×10^{-3}	-4.095×10^{-3}	-2.709×10^{-4}	9.722×10^{-5}	-5.443×10^{-5}				
Channel 1b, N ₂ Bath Gas									
1	8.686×10^{-1}	4.137	-5.246×10^{-1}	-1.804×10^{-1}	3.052×10^{-2}				
2	-3.640	-2.374×10^{-1}	-1.415×10^{-1}	2.495×10^{-2}	-1.687×10^{-2}				
3	-3.262×10^{-1}	-6.310×10^{-3}	1.286×10^{-2}	-5.535×10^{-4}	3.252×10^{-4}				
4	6.495×10^{-2}	8.846×10^{-3}	-1.900×10^{-3}	-1.990×10^{-4}	1.782×10^{-4}				
5	-7.880×10^{-3}	-4.176×10^{-3}	1.422×10^{-4}	1.760×10^{-4}	-6.227×10^{-5}				

^{*a*} Coefficients for use with with eq 31 of ref 49. Indexes *i* and *j* are for the reduced temperature and pressure, respectively. $T_{\min} = 800$ K, $T_{\max} = 3000$ K, $P_{\min} = 0.001$ atm, $P_{\max} = 100$ atm. The units of rate constants are s⁻¹.

conclusion is in agreement with the results of Besora and Harvey.⁸ However, the high-pressure limit is not reached even at the highest pressure used, 10⁵ Torr. Because of the falloff effects, the contribution of the singlet channel is significantly lower at realistic pressures. The switch between mostly triplet and mostly singlet products occurs at the pressures between 5000 and 20 000 Torr, depending on the temperature (Figure 4), and the share of the singlet channel drops below 10% at pressures below atmospheric for all temperatures considered.

The effects of uncertainties in the k(E) dependences of both channels on the thermal rate coefficients were estimated by comparing the rate constant values calculated using the limiting models with those obtained using the central model. The resultant uncertainty factors for the high-pressure-limit rate constants of the triplet channel (1a) are 1.7 at 800 K, 1.5 at 1000 K, and 1.2 at 2000–3000 K. For the singlet channel (1b), the upward and the downward uncertainty factors have different values because of the different estimated uncertainties in the energy barrier for this reaction channel (+8.4 kJ mol⁻¹, -2.0 kJ mol⁻¹). These factors for the high-pressure-limit rate constant of the reaction channel 1b are 3.5/1.3 at 800 K, 2.7/1.3 at 1000 K, 2.0/1.2 at 1500 K, 1.7/1.1 at 2000 K, and 1.4/1.1 at 3000 K (here and below, the first, larger factor is for the downward uncertainty). Under the falloff conditions, the uncertainty factors are more strongly dependent on pressure than on temperature. For channel 1a, the temperature-averaged uncertainty factors are 1.15-1.16 between 1 and 100 Torr, 1.4 at 1000 Torr, 2.0 at 10⁴ Torr, and 1.9 at 10⁵ Torr. For channel 1b, these factors are 210/29 at 1 Torr, 150/21 at 10 Torr, 58/11 at 100 Torr, 9.1/3.4 at 1000 Torr, 2.9/1.7 at 10⁴ Torr, and 2.2/1.4 at 10⁵ Torr. A detailed table of estimated uncertainty factors is given in the Supporting Information. As these numbers show, the estimated uncertainties are generally significantly larger for the singlet channel because its properties are based on quantum chemical calculations⁸ only. At the same time, the uncertainties in the properties of the triplet channel are considerably limited by the experimental data^{13,14} on the k(E) function, which is reflected in the low values of the uncertainty factors. It should be kept in mind that these uncertainty factors were estimated within the framework of the underlying computational model, which includes steady-state master equation for description of the falloff effects, temperature independent $\langle \Delta E \rangle_{\text{down}}$, and other features, as explained above.

To provide means for practical use of the calculated temperature and pressure dependences of the rate constants of the two channels of reaction 1, parametrization was performed. The traditional approach based on the high-pressure-limit and the low-pressure-limit modified Arrhenius expressions and the Troe broadening factor is inapplicable for reaction 1. Thus, parametrization based on the Chebyshev polynomial representation was used. The rate constants are expressed using the formalism of Venkatesh et al.⁴⁹ Coefficients $a_{i,i}$ given in Table 2 are to be used in eq 31 of ref 49, which provides the dependence of log (k) on reduced temperature and pressure. It is important to remember that the results of this parametrization cannot be used outside the specified ranges of temperature and pressure. Parameterization is provided for argon and nitrogen bath gases. In calculations, the value of $\langle \Delta E \rangle_{\text{down}}$ for nitrogen bath gas was taken as equal to that of argon, based on earlier studies of thermal decomposition of small polyatomic molecules (e.g., refs 50-52). This assumption introduces another uncertainty in the model.

The results on the channel branching obtained in the current work have implications for the kinetics of reactions that follow the initial decomposition of HN₃. Under the conditions of predominant formation of the singlet ¹NH biradical (very high pressures), its fast reaction with HN₃ (reaction 2b, Table 1 and ref 27) will results in quick formation of NH₂ and the N₃ radical, reactions of which will likely determine the subsequent overall kinetics. In the case of the dominating production of the triplet NH biradical, its reaction with HN₃ is significantly slower, which enables reactions of ³NH with itself and other radicals. These

reactions, in turn, can produce such reactive species as, for example, H and N atoms (reaction 3 and 4 in Table 1), which significantly complicates the mechanism of subsequent chemistry.

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Supporting Information Available: Values of $\langle \Delta E \rangle_{down}$ obtained in modeling experimental data, results of the rate constants calculations over wide ranges of temperatures and pressure, and the uncertainty factors due to model variations. This material is available free of charge via the Internet at http://pubs.acs.org.

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