Rate Constant and Branching Fraction for the $\text{NH}_2 + \text{NO}_2$ ReactionStephen J. Klippenstein,[†] Lawrence B. Harding,[†] Peter Glarborg,^{*,‡} Yide Gao,[§] Huanzhen Hu,[§] and Paul Marshall[§][†]Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, United States[‡]DTU Chemical Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark[§]Department of Chemistry, University of North Texas, 1155 Union Circle #305070, Denton, Texas 76203-5017, United States

Supporting Information

ABSTRACT: The $\text{NH}_2 + \text{NO}_2$ reaction has been studied experimentally and theoretically. On the basis of laser photolysis/LIF experiments, the total rate constant was determined over the temperature range 295–625 K as $k_{1,\text{exp}}(T) = 9.5 \times 10^{-7} (T/\text{K})^{-2.05} \exp(-404 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value is in the upper range of data reported for this temperature range. The reactions on the $\text{NH}_2 + \text{NO}_2$ potential energy surface were studied using high level ab initio transition state theory (TST) based master equation methods, yielding a rate constant of $k_{1,\text{theory}}(T) = 7.5 \times 10^{-12} (T/\text{K})^{-0.172} \exp(687 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in good agreement with the experimental value in the overlapping temperature range. The two entrance channel adducts H_2NNO_2 and H_2NONO lead to formation of $\text{N}_2\text{O} + \text{H}_2\text{O}$ (R1a) and $\text{H}_2\text{NO} + \text{NO}$ (R1b), respectively. The pathways through H_2NNO_2 and H_2NONO are essentially unconnected, even though roaming may facilitate a small flux between the adducts. High- and low-pressure limit rate coefficients for the various product channels of $\text{NH}_2 + \text{NO}_2$ are determined from the ab initio TST-based master equation calculations for the temperature range 300–2000 K. The theoretical predictions are in good agreement with the measured overall rate constant but tend to overestimate the branching ratio defined as $\beta = k_{1a}/(k_{1a} + k_{1b})$ at lower temperatures. Modest adjustments of the attractive potentials for the reaction yield values of $k_{1a} = 4.3 \times 10^{-6} (T/\text{K})^{-2.191} \exp(-229 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{1b} = 1.5 \times 10^{-12} (T/\text{K})^{0.032} \exp(761 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in good agreement with experiment, and we recommend these rate coefficients for use in modeling.

INTRODUCTION

The formation and consumption of nitrogen oxides (NO_x) at high temperatures continue to be an important area of research. Of particular interest is the chemistry of amine radicals. Ammonia is formed in significant quantities in devolatilization of solid fuels¹ and the selectivity in oxidation of amine radicals to form NO or N_2 is important for the yield of NO_x .² Reactions of amine radicals are also important for the performance of selective noncatalytic reduction (SNCR) of NO using amine-based additives such as ammonia or urea. In the past, both NH_3 oxidation^{2–6} and SNCR^{2,7–11} have been studied extensively within combustion.

Following the detection of NO_2 as an important intermediate in SNCR,¹² the reaction of NH_2 with NO_2 was identified as a key step.^{9,11} This reaction has two major product channels:

The prior analysis of Glarborg et al.¹³ provides an overall picture of the kinetics for this reaction. The NH_2 radical can add to either the N atom of NO_2 to form H_2NNO_2 or one of the O atoms to form H_2NONO . The H_2NNO_2 species ultimately produces $\text{N}_2\text{O} + \text{H}_2\text{O}$ (R1a) after a number of

isomerizations. Meanwhile, the H_2NONO species directly dissociates to $\text{H}_2\text{NO} + \text{NO}$ (R1b). Both of these sets of products are exothermic relative to reactants, and the transition states on the pathway to forming $\text{N}_2\text{O} + \text{H}_2\text{O}$ are all below the entrance channel. Thus, at least at low temperature, the rate coefficients are governed by the rates of adding the NH_2 to either the N or the O sites of NO_2 .

Values for both the overall rate constant^{13–22} and the branching fraction β , defined as $k_{1a}/(k_{1a} + k_{1b})$,^{13,14,20–25} have been reported over a wide range of conditions, but the scatter in the data is considerable. Measurements of the overall rate constant vary by an order of magnitude at 500 K.^{14,17,18} In addition, there appears to be some inconsistency in the low and high temperature measurements of the rate constant, with the recent high temperature data of Song et al.²² being substantially greater than expected from a simple extrapolation of the low temperature data. Also, the reported branching fraction values vary greatly; most determinations indicate a value of approximately 20%,^{13,21–25} but values of 65–95% have also been reported.^{14,20}

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The objective of the present work is 2-fold. First, we wish to provide a reliable set of rate coefficients for the $\text{NH}_2 + \text{NO}_2$ reaction and, if possible, resolve the experimental issues that have led to the unusually large spread in the reported rate parameters for this reaction. Second, the present analysis attempts to clarify a number of issues that have arisen in theoretical studies of this system. In particular, the theoretical analysis of Mebel et al.²⁶ indicates that there is a low lying transition state connecting the two entrance channel adducts (H_2NNO_2 and H_2NONO), while Glarborg et al.¹³ presumed that these pathways were unconnected. Incorporation of this saddle point in a master equation analysis suggests that $\text{H}_2\text{NO} + \text{NO}$ are the only products,²² whereas a variety of experimental studies have indicated that the branching to the $\text{N}_2\text{O} + \text{H}_2\text{O}$ channel is 20% or more.^{13,14,20–25} The study of Sun et al.²⁷ has ruled out the branching to a number of other possible channels. In the present work, the $\text{NH}_2 + \text{NO}_2$ reaction has been studied experimentally using laser photolysis/laser-induced fluorescence (LIF) and theoretically with high level ab initio transition state theory based master equation methods. The results are compared with data reported in the literature.

EXPERIMENTAL METHODOLOGY

NH_2 radicals were generated by pulsed laser photolysis of the NH_3 precursor (MG Industries, 99.99%, trapped and degassed at 77 K), and the radical concentration was monitored by LIF. General descriptions of the reaction cell and its operation have been provided elsewhere.^{28–31} The photolysis beam at 193 nm entered the reactor through quartz optics. The UV pulse energy F , together with $[\text{NH}_3]$ and its absorption cross-section³² yield the initial $[\text{NH}_2]$. Experiments were conducted in an Ar bath gas, which controlled the total pressure P , and with a large excess of NO_2 over NH_2 , typically in the range 10–50:1. The temperature T was measured with a thermocouple before and after each set of experiments. The NO_2 (Matheson, 99.5% purity) was purified by freeze–pump–thaw cycles at 77 K followed by several distillations from 178 K, before mixtures in Ar were prepared manometrically. Ar from Air Liquide (99.997% purity) was used directly from the cylinder. After a variable delay t from the photolysis pulse, a probe pulse with energy E from a Nd:YAG-pumped dye laser at 570.3 nm excited fluorescence from NH_2 .³³ This emission was passed through a blocking filter ($\lambda > 590$ nm), detected with a photomultiplier tube and recorded with a boxcar integrator. A typical plot of integrated fluorescence vs delay time after photolysis is shown in Figure 1. There was a constant background, which preliminary experiments showed to be present even in the absence of NH_2 .

Because $[\text{NH}_2]_0 \ll [\text{NO}_2]$, pseudofirst-order conditions apply and

$$\frac{d[\text{NH}_2]}{dt} = -(k_1[\text{NO}_2] + k')[\text{NH}_2] = -k_{\text{ps1}}[\text{NH}_2] \quad (1)$$

where k' accounts mainly for diffusional loss of NH_2 from the observation zone. All decays were observed to be exponential within the experimental uncertainty, and Figure 1 shows an exponential fit to the fluorescence decay plus constant background, which yields the pseudo-first-order decay coefficient k_{ps1} . A linear plot of this quantity vs $[\text{NO}_2]$ yields the total rate constant k_1 as the slope, and an example is shown in Figure 2.

Figure 1. Example of the integrated LIF signal intensity (arbitrary units) from NH_2 plus a constant background as a function of the delay time between the photolysis and probe lasers. The fit is an exponential decay. The conditions were $T = 296$ K, $[\text{NO}_2] = 2.5 \times 10^{13}$ molecules cm^{-3} , $P = 21$ mbar, $F = 0.4$ mJ, and $E = 0.35$ mJ.

Figure 2. Variation of the pseudofirst-order decay coefficients k_{ps1} for the removal of NH_2 as a function of the concentration of NO_2 , obtained at $T = 296$ K, $P = 21$ mbar, $F = 0.4$ mJ, and $E = 0.35$ mJ. The open symbol corresponds to the decay in Figure 1.

EXPERIMENTAL RESULTS

Thirty-one determinations of k_1 over 295–625 K are summarized in Table 1, along with the experimental conditions. We found no systematic variation of the observed k_1 with the average residence time of the reagent gases before photolysis, suggesting that there was no thermal NO_2/NH_3 chemistry under our conditions. The hydrogen atoms formed photolytically along with NH_2 may react quickly with NO_2 to make OH, whose reaction with NH_3 would regenerate NH_2 . Numerical simulations of our conditions using the comprehensive mechanism of Klippenstein et al.¹¹ with a modified $\text{H} + \text{NH}_2 + \text{M}$ recombination rate constant indicate reductions of the effective k_1 by around 10–20% at room temperature and 10% at 625 K. However, the absence of a systematic influence of

Table 1. Summary of Measurements of the Rate Constant k_1 for $\text{NO}_2 + \text{NH}_2$

T (K)	τ_{res} (s)	F^a (mJ)	E^b (mJ)	P (mbar)	$(10^{13} [\text{NO}_2]_{\text{max}})$ molecules cm^{-3}	$(10^{14} [\text{NH}_2]_{\text{max}})$ molecules cm^{-3}	$(10^{12} [\text{NH}_2]_0)$ molecules cm^{-3}	$k_1 \pm \sigma$, ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
293	0.8	0.2	0.7	11	1.83 ± 0.07	4.5	0.44	16.1 ± 0.93
293	0.8	0.2	0.9	12	1.85 ± 0.07	4.5	0.44	15.2 ± 1.05
294	0.8	0.4	0.4	12	2.59 ± 0.10	4.3	0.84	17.8 ± 1.13
294	0.8	0.2	0.4	12	2.59 ± 0.10	4.3	0.42	18.5 ± 0.92
295	0.8	0.8	0.9	12	4.89 ± 0.20	5.3	2.06	15.2 ± 0.87
295	0.7	0.4	0.9	12	6.64 ± 0.27	8.3	1.61	15.7 ± 0.64
296	1.5	0.4	0.9	20	9.39 ± 0.38	9.6	1.86	16.5 ± 1.05
296	0.6	0.4	0.4	21	3.42 ± 0.14	4.3	0.84	16.7 ± 0.71
296	0.8	0.4	0.4	12	3.96 ± 0.16	4.3	0.84	17.3 ± 1.22
								20.6 ± 1.10^c
385	0.6	0.4	0.9	12	6.65 ± 0.27	6.3	1.22	12.6 ± 0.84
386	0.6	0.4	0.9	14	4.88 ± 0.20	6.6	1.28	10.7 ± 0.73
393	0.5	0.4	0.5	13	3.56 ± 0.14	4.5	0.87	12.1 ± 0.95
393	0.5	0.8	0.5	14	2.86 ± 0.11	4.5	1.75	10.1 ± 0.61
400	0.5	0.2	0.3	13	2.86 ± 0.11	4.5	0.44	14.9 ± 0.79
400	0.5	0.2	0.6	13	2.86 ± 0.11	4.5	0.44	11.7 ± 0.56
								16.1 ± 0.98^c
486	0.4	0.4	0.3	14	3.37 ± 0.13	6.5	1.26	10.2 ± 0.85
492	0.5	0.4	0.3	12	6.13 ± 0.25	5.3	1.03	9.6 ± 0.63
512	0.4	0.2	0.3	13	1.86 ± 0.07	6.0	0.58	9.66 ± 0.51
512	0.4	0.2	0.6	14	1.86 ± 0.07	6.0	0.58	8.67 ± 0.47
514	0.5	0.8	0.9	12	2.64 ± 0.11	5.6	2.18	7.17 ± 0.35
516	0.5	0.4	0.3	12	3.4 ± 0.14	5.7	1.11	10.7 ± 0.48
526	0.5	0.8	0.9	12	1.81 ± 0.07	4.3	1.67	6.17 ± 0.37
526	0.4	0.4	0.5	15	1.43 ± 0.06	4.6	0.89	9.39 ± 0.55
								11.9 ± 0.76^c
622	0.3	0.4	0.7	15	2.03 ± 0.08	4.4	0.86	7.1 ± 0.39
622	0.3	0.8	0.9	15	1.36 ± 0.05	4.4	1.71	4.91 ± 0.31
623	0.4	0.4	0.9	12	1.33 ± 0.05	5.9	1.15	5.49 ± 0.28
623	0.4	0.4	0.5	12	0.77 ± 0.03	5.9	1.15	7.92 ± 0.25
626	0.3	0.4	0.9	16	1.57 ± 0.06	6.0	1.17	5.44 ± 0.31
627	0.4	0.4	0.5	13	2.54 ± 0.10	5.7	1.11	7.33 ± 0.29
628	0.3	0.4	0.7	13	2.38 ± 0.10	4.7	0.91	7.08 ± 0.32
628	0.3	0.4	0.9	11	1.08 ± 0.04	5.6	1.09	5.84 ± 0.24
								9.10 ± 0.41^c

^aPhotolysis energies for NH_3 . ^bDye laser energies for LIF of NH_2 . ^cExtrapolation to zero dye laser energy.

photolysis energy F and initial $[\text{NH}_2]$ would indicate that reaction 1 was successfully isolated from secondary chemistry. Possibly the initial radical concentrations are smaller than estimated here. To be cautious, we allow for the potential secondary chemistry in our error limits. There is a modest systematic trend of k_1 with the energy of the probe beam E . Higher values of E yielded lower values of k_1 . We speculate this may be an artifact arising from possible emission from NO_2 , which can also absorb light at 570.3 nm. Accordingly, at each temperature we extrapolated the measured k_1 values linearly to zero E (these plots are included in the Supporting Information), and these results are also shown in Table 1. The quoted uncertainties reflect the statistical uncertainties in the intercepts of the k_1 vs E plots. These extrapolated data are plotted in Arrhenius form in Figure 3 and can be summarized over 295–625 K as

$$k_1(T) = 9.5 \times 10^{-7} (T/\text{K})^{-2.05} \exp(-404 \text{ K}/T) \\ \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Overall error limits for k_1 are considered to be about 20%, based on propagation of instrumental uncertainties, and

Figure 3. Arrhenius plot of the measured overall rate constant for the $\text{NH}_2 + \text{NO}_2$ reaction.

allowance for uncertainty in the extrapolations and possible secondary chemistry.

Figure 4 compares the present experimental data for the overall rate with results from literature, as well as with the

Figure 4. Plot of the temperature dependence of the overall rate constant for the reaction of NH_2 with NO_2 . “This Work” denotes the present theoretical rate constant, while “Present” denotes the experimental results obtained in the present study. Literature data: Glarborg,¹³ Song,²² Xiang,¹⁷ Pagsberg,¹⁹ Whyte,¹⁶ Hack,¹⁴ Bulatov,¹⁸ and Kurosawa.¹⁵

theoretical rate constant discussed in the next section. The present measurements are in close accord with the results of Kurosawa and Lesclaux who employed a similar pulsed-photolysis LIF technique¹⁵ over a range of temperatures, and there is good agreement with the room temperature LIF data of Whyte and Phillips¹⁶ and Xiang et al.¹⁷ The LIF results from Hack et al.¹⁴ lie a factor of 2–4 below other studies, and apparently, some unrecognized interference was present. By contrast to the present LIF work, experiments based on optical absorption should not be sensitive to the intensity of the probe beam, and the results of Bulatov et al.¹⁸ and Pagsberg et al.¹⁹ agree with the present work at room temperature. The temperature dependence obtained by Bulatov et al. is somewhat

more negative than measured here, leading to a difference of about a factor of 1.5 at 600 K.

Theoretical. As discussed in the Introduction, the NH_2 radical can add to either the N or O atoms in NO_2 to form H_2NNO_2 or H_2NONO , respectively. Glarborg et al.¹³ presumed that these pathways were unconnected, while Mebel et al.²⁶ found a low lying transition state connecting the two entrance channel adducts (H_2NNO_2 and H_2NONO). More recently, Song et al.²² did a master equation analysis of the reaction, based on a slightly modified version of the potential energy surface obtained by Mebel et al., with the overall rate constant adjusted to agree with experiment. According to their analysis, $\text{H}_2\text{NO} + \text{NO}$ are the only products, in disagreement with a large body of experimental results.

In the present work, we apply advanced ab initio transition state theory based master equation methods to the analysis of the full temperature and pressure dependence of the kinetics. A key feature of the analysis involves the treatment of the various barrierless channels involved in the overall kinetics with the direct variable reaction coordinate (VRC)-TST method,^{34–37} as discussed below. To begin, we have recalculated the energies of the stationary points with two methods. First, we applied the RQCISD(T)/CBS(QZ,SZ)//B3LYP/6-311++G(d,p) method. The complete basis set (CBS) analysis is based on a two-point $1/(l+1)^4$ extrapolation of explicit calculations with Dunning’s cc-pVQZ and cc-pVSZ basis sets.³⁸ Subsequently, we have obtained higher level (HL) estimates through the combination of a UCCSD(T)/cc-pVTZ rovibrational analysis with UCCSD(T)/CBS(aug-cc-pVQZ’, aug-cc-pVSZ’) energies, CCSDT(Q)/cc-pVDZ higher order corrections, CCSD(T,full)/CBS-(TZ,QZ) core–valence corrections, CI/aug-cc-pcVTZ relativistic corrections, HF/cc-pVTZ diagonal Born–Oppenheimer corrections, and B3LYP/6-311++G(d,p) anharmonic ZPE corrections. This method is closely related to other high level methods such as the popular HEAT³⁹ and W4⁴⁰ methods, for example.

The anharmonic ZPE correction is calculated as the difference between spectroscopic perturbation theory and

Table 2. Stationary Point Energies for the Reaction of NH_2 with NO_2 ^a

species	G2(Pu) ^b	CBS-Q ^c	RQCISD(T)/CBS	HL	PT2/CBS
$\text{NH}_2 + \text{NO}_2$	0		0	0	0
H_2NNO_2 (1)	−52.0		−50.40	−49.90	
H_2NONO (2)	−34.1	−30.9	−31.70	−30.80	
<i>trans</i> -HNN(O)OH (3)	−42.6	−40.9	−41.47	−41.04	
<i>cis</i> -HNN(O)OH (4)		−40.7	−41.30	−40.78	
$\text{H}_2\text{NO} + \text{NO}$ (P1)	−13.3		−15.35	−14.35	
$\text{H}_2\text{O} + \text{NNO}$ (P2)	−91.0		−90.96	−90.55	
<i>trans</i> -HNNO + OH (P3)	9.5		5.46	4.93	
<i>cis</i> -HNNO + OH (P4)	15.0		11.33	11.20	
$^3\text{NH} + \text{HONO}$ (P5)			14.16	14.31	
(1) ↔ (3)	−12.5	−12.3	−12.58	−11.62	
(3) ↔ (4); bend	−8.5	−14.9	−15.68	−14.67	
(3) ↔ (4); torsion	−3.4		−10.87	−9.96	
(4) ↔ (P2)	−5.3	−10.7	−10.81	−10.26	
$\text{NH}_2 + \text{NO}_2 \leftrightarrow$ (P1)			32.10		
$\text{NH}_2 + \text{NO}_2 \leftrightarrow$ (P5)			22.09		
$\text{H}_2\text{N} \cdots \text{N}(\text{O})\text{O} \leftrightarrow \text{H}_2\text{N} \cdots \text{ONO}$					−1.13

^aAll energies include zero-point corrections and are in kcal/mol relative to $\text{NH}_2 + \text{NO}_2$. ^bFrom Mebel et al.²⁶ ^cFrom Ploeger et al.⁵¹ using the present H_2NNO_2 HL result as a reference since they do not provide the energy of $\text{NH}_2 + \text{NO}_2$.

harmonic results, both obtained at the B3LYP/6-311++G(d,p) level. For simplicity, and due to inherent inaccuracies in spectroscopic perturbation theory at high temperatures, the B3LYP anharmonic analysis is employed solely to generate ZPE corrections, and the CCSD(T)/cc-pVTZ harmonic frequencies are used in the evaluations of the partition functions. This simplification should be satisfactory given that the anharmonic vibrational effects on the partition function would largely cancel in taking the ratio of the transition state and reactant partition functions.

With the exception of the B3LYP anharmonic analyses, which were performed with Gaussian09,⁴¹ and the HF/cc-pVTZ diagonal Born–Oppenheimer corrections, which were obtained with CFOUR,⁴² all the electronic structure calculations were performed with MOLPRO.^{43,44} The aug-cc-pVQZ' basis sets employed here are a modification of the aug-cc-pVNZ sets of Kendall et al.,⁴⁵ which, for the diffuse part of the basis, retains only that corresponding to the valence shell. The CCSDT(Q)⁴⁶ higher order corrections were obtained with Kallay's MRCC supplement⁴⁷ to MOLPRO. The core–valence corrections employ the cc-pCVnZ basis sets of Dunning and Woon.⁴⁸ The relativistic corrections were obtained with the Douglas–Kroll Hamiltonian.⁴⁹

The present high level (HL) method has two sigma uncertainties for heat of formation values on the order of 0.3 kcal/mol (in comparisons with a large set of Active Thermochemical Tables (ATcT) values⁵⁰), while the RQCISD-(T)/CBS method has uncertainties of ~ 1 kcal/mol. The HL uncertainties for saddle points may be somewhat larger, but this is yet to be determined. Limited evidence suggests they are still on the order of ~ 0.3 kcal/mol or less, at least when multireference effects are not substantial.

The present predictions for the stationary point energies are tabulated in Table 2 together with those from two earlier theoretical studies.^{26,51} For this system, the HL method has the effect of raising (relative to the RQCISD(T)/CBS results) essentially all of the stationary points relative to the reactants $\text{NH}_2 + \text{NO}_2$. For the minima, this shift is typically 0.5 kcal/mol, while for the saddlepoints it is about 1.0 kcal/mol. The bimolecular products $\text{HNNO} + \text{OH}$ are an exception to this rule, with these products instead shifted down by 0.5 kcal/mol. The primary effect is a reduction in the rate coefficient for forming $\text{H}_2\text{O} + \text{N}_2\text{O}$ (relative to our preliminary RQCISD(T)/CBS results). Notably, this results in improved agreement with experiment for both the total rate coefficient and the branching ratio.

A schematic diagram of the HL potential energy surface is provided in Figure 5. This potential energy surface is reminiscent of that for $\text{NH}_2 + \text{NO}$, where all the NH bonds are broken and replaced by OH bonds. For completeness, we have also considered a few additional channels that might contribute at higher temperatures. In particular, we have considered the dissociations of the *cis*- and *trans*-HNN(O)OH isomers to *trans*- and *cis*-HNNO + OH, respectively, as in the work of Mebel et al.²⁶ At high energies these channels begin to compete effectively with the $\text{H}_2\text{O} + \text{N}_2\text{O}$ loss channel, due to their much greater transition state entropies. We have also considered the direct abstractions to yield $^3\text{NH} + \text{HONO}$ or $\text{H}_2\text{NO} + \text{NO}$, which also might play a role at high temperature. However, these channels were found to be insignificant at least for temperatures of 2000 K and lower.

The transition state connecting H_2NNO_2 with H_2NONO requires some further discussion, and it is helpful to begin by

Figure 5. Schematic plot of the potential energy surface for the reaction of NH_2 with NO_2 . The primary paths for the addition to the N and O sides are highlighted in red and dark blue, respectively. The roaming path, which connects the N and O adducts, is highlighted in light blue. For the *cis*- to *trans*-HNN(O)OH isomerization, the red solid line denotes an in-plane bending path, while the dotted black line denotes a torsional path.

reviewing the general picture that has developed for the related isomerizations of RONO_2 to ROONO species.⁵² The potential for these reactions has been considered in great detail for $\text{R} = \text{H}$ and CH_3 , for example.^{53–55} Notably, for such reactions, the tight transition state connecting the two species is predicted to lie at energies that substantially exceed the threshold to formation of $\text{OR} + \text{NO}_2$. This high barrier has presented a great conundrum for atmospheric chemists trying to understand the forward and backward isomerizations between RONO_2 and ROONO and the corresponding bimolecular products. Ultimately, a likely solution was found in the presence of a low energy roaming process,⁵⁶ where the OR nearly dissociates from the RONO_2 species, then roams to the O side of NO_2 , where it reattaches to form ROONO .^{52,57} As expected, the energy of this roaming transition state is close to the $\text{OR} + \text{NO}_2$ threshold.

The transition state of Mebel et al.²⁶ contradicts this picture, with a low energy tight transition state connecting the two species for $\text{OR} = \text{NH}_2$. It is difficult to see why this tight transition state should be so different from that for the isoelectronic OH and CH_3 species. Our attempt to reproduce Mebel's results leads to a transition state that actually corresponds to a *cis*–*trans* isomerization in H_2NONO , as demonstrated through reaction path following. Furthermore, Soto and co-workers have employed multireference methods in the study of the H_2NNO_2 to H_2NONO isomerization and come to similar conclusions.⁵⁸ Thus, it appears that the analysis of Mebel et al. mistakenly attributed this torsional isomerization TS to the H_2NNO_2 to H_2NONO conversion TS.

We have used the CASPT2(2e,2o)/aug-cc-pVTZ method⁵⁹ to explore the roaming reaction path for this reaction. We find a saddle point at -1.13 kcal/mol (at the CASPT2/CBS-(AQZ,ASZ) level after ZPE correction) for the NH_2 group rotating relative to the plane of NO_2 as illustrated in Figure 6. Following the intrinsic reaction coordinate path at the CASPT2(2e,2o)/aug-cc-pVDZ level from this saddle point leads to the H_2NNO_2 complex in one direction and to a long-range complex where the NH_2 group is on the back side of the ONO fragment in the other direction. Because of limitations in the (2e,2o) active space, this complex does not relax directly to H_2NONO . Nevertheless, larger active spaces remove the barrier of the addition to the O end of ONO, and it seems clear that this roaming saddle point is properly connected to

Figure 6. Illustration of the stationary point structures for the roaming pathway. Red, blue, and white denote O, N, and H atoms, respectively.

H₂NONO. Soto and co-workers also searched for roaming saddlepoints with larger active space CASPT2 calculations.⁵⁸ Their search instead found a conical intersection related to the isomerization of the *cis*-H₂NONO. It is not clear whether they searched for the out-of-plane pathway to the *trans*-isomer that we report here.

For the NO + H₂NO exit channel, one might at first glance expect some roaming induced branching to HNO + HNO since NO and H₂NO are both radicals and HNO is a closed shell molecule. However, the HNO + HNO product channel is actually higher than NO + H₂NO, in which case roaming is not expected to be significant.

The following analysis considers the pathways via H₂NNO₂ and H₂NONO to be uncoupled. In reality, there is some coupling through the aforementioned roaming pathway. However, prior theoretical and experimental studies indicate that for the dissociations of acetaldehyde and dimethyl ether^{56,60,61} such roaming radical pathways constitute only a small fraction (~10–20% or less) of the dissociation flux. For the present reactions, one might similarly expect only a modest perturbation of the predicted entrance branching by such roaming pathways, especially at the high temperatures of combustion. A limited study, implementing a 6 well kinetic scheme with two long-range complexes and assuming rapid roaming, validated this thought. The perturbations on the branching ratios were a few % at most, while the effect on the overall rate was similarly small but hard to determine due to changes from a single TS to a 2 TS picture. It does not seem worth pursuing further here.

We have implemented direct VRC-TST calculations for the five barrierless radical–radical channels in our schematic PES (cf. Figure 5) for the NH₂ + NO₂ reaction system. Three of these systems (NH₂ + NO₂ → H₂NNO₂; NH₂ + NO₂ → H₂NONO; H₂NONO → H₂NO + NO) involve rather complex interactions that are not well described with small active space CASPT2 evaluations. In contrast, CAS+1+2+QC calculations with a simple two-electron two-orbital (2e,2o) active space do provide a fairly accurate reproduction of calculations with larger active spaces along the minimum energy paths. This active space and method was employed for the two NH₂ + NO₂ addition channels. For the H₂NO + NO channel, a CAS+1+2+QC approach with a (6e,5o) active space and a 2-state orbital averaging was required due to wave function convergence problems related to the degeneracy of the NO orbitals at infinite separation. This (6e,5o) active space consisted of the (5e,4o) π -space of NO and the NH₂ radical orbital. For the OH additions to *cis*- and *trans*-HNNO, CASPT2(6e,5o) calculations were found to be adequate, where the active orbitals correlate with the (3e,2o) π -space of OH and the (3e,3o) π -space of HNNO. The orbitals in these calculations were averaged over the two states correlating with the degenerate states of OH.

The orientational sampling for the two NH₂ + NO₂ addition channels employed the cc-pVTZ basis set, while the cc-pVDZ basis was employed for the H₂NO + NO channel and the aug-cc-pVDZ basis set was employed for the *cis*- and *trans*-HNNO + OH channels. The separation between the additions to the N and O sides in the NH₂ + NO₂ reaction is accomplished through the implementation of a presumed infinite potential perpendicular to the C_{2v} axis of NO₂. Approximate boundary potentials were also used to separate the additions to the O side of H₂NO and the central N of HNNO, for the NO + H₂NO and OH + HNNO additions, respectively. A dynamical correction factor of 0.85 is also incorporated. This correction factor accounts for the small degree of recrossing of the variable reaction coordinate transition state dividing surfaces as estimated in prior work for related reactions.⁶²

One-dimensional correction potentials were employed to approximately account for the limitations in the basis set, in the active space, and for geometry relaxation. The basis set corrections were obtained from CBS extrapolations based on explicit calculations with cc-pVTZ and cc-pVQZ basis sets. For the NH₂ + NO₂ addition channels, the active space corrections were obtained from calculations with a (10e,7o) active space consisting of a (9e,6o) active space for NO₂ and the radical orbital for NH₂. Meanwhile, the geometry relaxation corrections were obtained from full and partial optimizations with the PT2(6e,5o)/cc-pVTZ and CAS+1+2+QC(8e,6o)/cc-pVTZ methods for the N and O additions, respectively. For the H₂NO + NO case, the geometry relaxation correction is obtained from CAS+1+2+QC(6e,5o)/aug-cc-pVDZ calculations. The geometry relaxation correction was very small for the H₂NNO₂ case but is a very significant component of the interaction energy for both the formation and decomposition of H₂NONO. For the OH + HNNO reactions, the PT2(6e,5o)/adz geometry relaxation and CBS corrections were found to be negligible, and so, no correction was included.

The final interaction energies along approximate minimum energy paths are illustrated in Figure 7 for the various radical–radical reaction channels. These approximate minimum energy paths correspond to radial scans for a fixed angle of attack that correlates with the optimal orientation in the transition state region. The interactions for the formation and decomposition of H₂NONO and H₂NNO₂ are relatively weak compared with

Figure 7. Plot of the interaction energy along approximate minimum energy paths for the addition of (i) NH₂ to the N end of NO₂, (ii) the O end of NO₂, (iii) NO to the O atom in H₂NO, and (iv) OH to the N atom in *trans*-HNNO.

those for simple hydrocarbon radical–radical reactions due to the need to break resonances in the radicals during the bond formation process. The interactions in the HNNO + OH case are more typical. The interactions in the H₂NO + NO case are extraordinarily weak due to the need to break the resonance in both the H₂NO and the NO radicals. The N atom in NO₂ has more radical character than the O atoms, which correlates with the increased attraction for the addition to the N atom.

For the addition of NH₂ to the N and O atoms in NO₂ we have also evaluated the variation in the frequencies along distinguished coordinate minimum energy paths (MEP) using the B3LYP/6-31G* method. These frequencies are used to obtain harmonic quantum corrections for the transitional modes given by the ratio of the quantum harmonic oscillator canonical partition functions to the classical harmonic oscillator partition functions. These corrections are evaluated at the canonical transition state locations and yield reductions of about 10 to 20%, with the correction greatest for the O addition case. These frequencies also allow us to evaluate reaction coordinate-dependent conserved mode partition function corrections. However, the latter corrections are found to be insignificant.

The transitional mode quantum correction is likely also significant for the H₂NO + NO case, especially given the even weaker attractiveness for the MEP. However, the formation of H₂NO + NO is not rate limiting for the NH₂ + NO₂ kinetics, even for its branching, and so we do not pursue that further here.

The dynamically corrected VRC-TST predictions for the high pressure capture rate coefficients are illustrated in Figure 8.

Figure 8. Plot of the predicted high pressure capture rates for the radical–radical channels involved in the NH₂ + NO₂ reaction system.

Notably, the predicted rate constants are all relatively small, and those for NH₂ + NO₂ decrease significantly with increasing temperature. These effects are closely related to the weakness of the interaction energies along the minimum energy path. For the HNNO + OH reaction, the rate coefficient is relatively small due to our focus on only the addition to the central N atom. The total rate constant would be significantly greater. The relatively weak interaction energies also imply increased uncertainties in our predictions, particularly at low temperature. We crudely estimate these uncertainties as a factor of 1.4, 1.6, 2, 2, and 2 for the NH₂ + NO₂ → H₂NNO₂, NH₂ + NO₂ → H₂NONO, *cis*-HNNO + OH → *trans*-HNN(O)OH, *trans*-HNNO + OH → *cis*-HNN(O)OH, and H₂NO + NO → H₂NONO reactions, respectively. For the HNNO + OH case,

these uncertainties are increased due to uncertainties in the separation into distinct addition sites, with these uncertainties being particularly large at low temperature.

The calculated VRC-TST fluxes are combined with conventional rigid-rotor harmonic oscillator TST estimates for the remaining channels to obtain master equation based predictions for the pressure-dependent rate coefficients. The quantum corrections are difficult to incorporate precisely for the H₂NNO₂ case since they are canonical corrections and the simulations require microcanonical corrections. For simplicity we just include a constant correction to the entrance number of states of 0.92, which correlates with the magnitude of the correction in the 300–600 K temperature regime. For the H₂NONO case, we can directly use the canonical correction since all the entrance flux proceeds to products.

The low pressure limit rate coefficient for the formation of H₂NO + NO is essentially identical to the high pressure rate constant to form H₂NONO. In contrast, the ratio of the high pressure rate coefficient to form H₂NNO₂ to the sum of the low pressure rate coefficients for the formation of the other bimolecular products deviates significantly from unity. It increases with temperature reaching a factor of 10 at 1500 K. Nevertheless, we predict there to be little pressure dependence to the reaction for pressures below 100 atm because the complex lifetimes are too short to permit significant collisional relaxation for all but very low temperatures and high pressures.

The high and low-pressure limit rate constants are reproduced accurately over the 300–2000 K temperature range by the following modified Arrhenius expressions (cm³ molecule⁻¹ s⁻¹):

$$k^\infty = 7.52 \times 10^{-12} T^{-0.172} \exp(687/T)$$

$$k^\infty = 8.69 \times 10^{-12} T^{-0.033} \exp(315/T)$$

$$k_0 = 1.17 \times 10^{-5} T^{-2.317} \exp(-202/T)$$

$$k_0 = 5.81 \times 10^{-10} T^{-0.927} \exp(-2735/T)$$

$$k_0 = 3.72 \times 10^{-12} T^{-0.093} \exp(-5640/T)$$

$$k^\infty = 3.99 \times 10^{-13} T^{0.191} \exp(786/T)$$

$$k_0 = 3.99 \times 10^{-13} T^{0.191} \exp(786/RT)$$

$$k^\infty = 3.50 \times 10^{-17} T^{1.382} \exp(824/T)$$

$$k^\infty = 2.04 \times 10^{-12} T^{0.107} \exp(90.1/T)$$

$$k^\infty = 2.08 \times 10^{-12} T^{0.121} \exp(146/T)$$

where T is in K. These predictions are compared with the prior experimental and theory/modeling results for the total rate coefficient^{13–19,22} in Figure 4 and for the branching ratio^{13,20–25} in Figure 9. The present theoretical predictions

Figure 9. Plot of the temperature dependence of the branching ratio for production of $\text{N}_2\text{O} + \text{H}_2\text{O}$ in the reaction of NH_2 with NO_2 . The experimental results are all for the branching to $\text{N}_2\text{O} + \text{H}_2\text{O}$ ($\beta = k_{1a}/(k_{1a} + k_{1b})$), while the theoretical results are for the channel as noted in the legend. Literature data: Glarborg,¹³ Park,^{21,23} Meunier,²⁰ Quandt,²⁴ Lindholm,²⁵ and Song.²²

for the overall rate constant are seen to be in good agreement with our experimental results, but are about a factor of 3 lower than the high-temperature results of Song et al.²² The branching to the HNNO + OH channels, of minor significance at high temperatures, is clearly not sufficient to explain this discrepancy. Note that, because the $\text{NH}_2 + \text{NO}_2$ reaction occurs in the low pressure limit, the expressions for the various recombination processes are not needed to model this reaction process. Nevertheless, they may prove useful in other studies and so are reported here.

The predictions for the branching to $\text{N}_2\text{O} + \text{H}_2\text{O}$ tend to be greater than the experimental observations, particularly at low temperature where the discrepancy is almost a factor of 2. However, there is one low temperature measurement of the branching ratio that is greater than our predictions. At high temperature the predicted branching is in good agreement with the experiments of Song et al., while the prior theoretical work of Glarborg et al. also agrees quite well. Interestingly, a roaming from H_2NNO_2 to H_2NONO might be thought to provide some reduction in the low temperature branching to $\text{N}_2\text{O} + \text{H}_2\text{O}$. However, as discussed above, our sample calculations indicate that this is not feasible because the H_2NNO_2 simply proceeds on to $\text{H}_2\text{O} + \text{NNO}$ too rapidly for roaming to be competitive with it, especially at low temperature.

There is considerable uncertainty in the present theoretical predictions due to the relatively weak interactions along the MEP for the barrierless channels. Thus, we have explored the sensitivity of the predictions to these values with some simple calculations. First, we have increased by 20% the attractiveness of the potential for the addition to the O side of NO_2 to form H_2NONO .⁶³ The resulting predictions for the total rate constants are plotted in Figure 10. Notably, while this does increase the predicted rate constant, they are still about a factor

Figure 10. Arrhenius plot of the temperature dependence of the overall rate constant for the reaction of NH_2 with NO_2 for the reference potential and for a 20% increase in the attractiveness of the potential for the addition to form H_2NONO .

of 2 lower than the Song et al. values and are then much too high at low temperature. This level of change is close to the maximum reasonable. Similar changes in the potential for the addition to form $\text{H}_2\text{NN(O)O}$ have a negligible effect at the temperatures of the Song et al. experiments because the subsequent isomerizations provide the primary reactive bottleneck for that side. Furthermore, the effect of those isomerization bottlenecks is relatively insensitive to reasonable variations in the barrier heights since those barriers already lie well below reactants. Thus, it is hard to reconcile the present theoretical predictions with the rate values of Song et al.

Notably, similar magnitude changes in the attractive potentials yield markedly improved agreement for the low temperature branching ratios. In particular, increasing the attractiveness for the O side addition by 6% and decreasing the attractiveness for the N side addition by 18% yields the predicted branching ratio illustrated in Figure 11. This branching ratio is reasonably well reproduced by the expression $\beta = 3.92 \times 10^5 (T/\text{K})^{-1.984} \exp(-893 \text{ K}/T)$ over the 300 to

Figure 11. Branching ratio predictions with potential for the addition to the O side 6% more attractive than reference and the addition to N side 18% less attractive.

2000 K temperature range. With this revision the predicted branching ratios are in satisfactory agreement with experiment throughout the experimentally studied temperature region, and the predicted total rate coefficient has only increased by about 10%. Importantly, the chemical interactions for the N and O additions are entirely different and so a differential sign for the change in the attractiveness is not unwarranted. Furthermore, changes on the order of 10–20% are quite reasonable. The relatively strong dependence of the branching fractions on these parameters is related to the relative weakness of the attractive potential as compared to other simple radical–radical recombinations.

With this revision, the individual rate constants are given by

$$k_{1a} = 4.32 \times 10^{-6} T^{-2.191} \exp(-229/T)$$

$$k_{1b} = 1.51 \times 10^{-12} T^{0.0321} \exp(761/T)$$

$$k_{1c} = 5.57 \times 10^{-10} T^{-0.926} \exp(-2756/T)$$

$$k_{1d} = 3.96 \times 10^{-12} T^{-0.107} \exp(-5655/T)$$

where T is in K. These values are recommended for use in modeling.

The branching ratio β also depends to some extent on the properties of the tight transition states connecting H_2NNO_2 to the bimolecular products $\text{H}_2\text{O} + \text{N}_2\text{O}$. However, at least the barrier height sensitivity is small because of the expected high accuracy of our ab initio energies, coupled with the fact that all the barriers are submerged well below the reactants energy. Uncertainties in the transition state partition functions may be more significant. Notably, the CCSD(T)/cc-pVTZ frequencies employed here are expected to be quite accurate and so the largest partition function uncertainties arise from inaccuracies in the rigid-rotor harmonic oscillator assumptions. Overall, the uncertainties in the tight TS partition functions are perhaps on the order of a factor of 1.5.

Analysis of High-Temperature Data. As discussed in the Introduction, the $\text{NH}_2 + \text{NO}_2$ reaction attains its largest practical importance in the SNCR process, which is active in the 1000–1400 K range. The only data obtained at higher temperatures were reported by Glarborg et al.¹³ (850–1350 K) and Song et al.²² (1320–1530 K). Both of these studies indicated a total rate constant larger than the one reported in the present work and a branching fraction β of about 20%. However, in both high-temperature studies the NH_2 radicals were generated thermally. In this way, the chemistry involved became more complex due to secondary reactions, and the experimental data required interpretation in terms of a complex chemical kinetic model. Even though this approach has provided accurate data for the rate constant and branching fraction of the related $\text{NH}_2 + \text{NO}$ reaction,^{64,65} results would be expected to be more uncertain.

Song et al.²² used thermal dissociation of benzylamine in a reflected shock tube to generate NH_2 radicals in large excess of NO_2 and then monitored the NH_2 concentration as a function of time. The overall rate constant k_1 was determined by fitting

the computed and observed NH_2 profile, using a 118 step reaction mechanism. Their reported sensitivity analysis indicates that the NH_2 profile is mostly sensitive to k_1 and to the rate constant for the thermal dissociation of $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ to yield NH_2 . Comparison with the results of the present work, as well as data from other studies, indicate that the value of k_1 derived this way by Song et al. is too high by a factor of 2–3, but the cause of the discrepancy is not clear. We tend to attribute the high value of k_1 to complexities in the benzylamine dissociation chemistry, rather than in the NH_2/NO_2 reaction subset, and do not analyze these data further in the present work.

Instead, we have chosen to reinterpret the flow reactor results of Glarborg et al.¹³ Their experiments were carried out with $\text{NH}_3/\text{NO}_2/\text{N}_2$ mixtures, with trace impurities of NO (about 10% of the total nitrogen oxides), O_2 , and H_2O . Our understanding of the NH_3/NO_x chemistry has improved significantly¹¹ since the work of Glarborg et al., and it is of interest to evaluate whether the changes have implications for the interpretation of their experimental results.

Figure 12 shows comparison between selected experimental results of Glarborg et al. and model predictions with a detailed

Figure 12. Comparison of experimental data and modeling predictions for the NH_3/NO_2 system. Experimental data from Glarborg et al.¹³ The modeling is conducted with the reaction mechanism of Klippenstein et al.¹¹ except for the $\text{NH}_2 + \text{NO}_2$ reaction where the rate constants for the four product channels are taken from the present work (solid line). In addition, calculations are shown for values of the branching fraction ($\beta = k_{1a}/(k_{1a} + k_{1b})$) of 10% (short-dashed line) and 20% (long-dashed line). Inlet concentrations: $\text{NH}_3 = 492$ ppm, $\text{NO}_2 = 515$ ppm, $\text{NO} = 60$ ppm, H_2O and O_2 trace concentrations; balance N_2 . Residence time = $104/T$ sec (T in Kelvin); pressure = 1.05 atm.

chemical kinetic model. The modeling is conducted with the reaction mechanism of Klippenstein et al.,¹¹ except for the $\text{NH}_2 + \text{NO}_2$ reaction. For this step, we have used the rate constants $k_{1a} - k_{1d}$ from the present work (shown as solid lines). In addition, calculations are shown for values of the branching fraction ($\beta = k_{1a}/(k_{1a} + k_{1b})$) of 10 and 20% (shown as dashed lines). In addition to $\text{NH}_2 + \text{NO}_2$, the mechanism of Klippenstein et al. involves more accurate rate constants for the $\text{NH}_2 + \text{NO}$ reaction, as well as for reactions of NNH , compared to the original scheme of Glarborg et al.

Despite the absence of oxygen in the inlet gas, reaction occurs at temperatures as low as 850 K (Figure 12). Consumption of NH_3 and NO_2 increases only slowly with temperature up to 1350 K. NO_2 is converted primarily to NO , with minor amounts of N_2O formed. A nitrogen balance shows that N_2 constitutes less than 10% of the nitrogen pool at 900 K, increasing up to about 30% at 1350 K. The detection of N_2O among the products, even at temperatures as low as 850 K, supports the occurrence of the $\text{N}_2\text{O} + \text{H}_2\text{O}$ channel (R1a) of the $\text{NH}_2 + \text{NO}_2$ reaction. However, most of the NH_3 and NO_2 are converted to NO , consistent with $\text{H}_2\text{NO} + \text{NO}$ (R1b) being the dominating product channel.

As discussed by Glarborg et al.,¹³ the key reaction is $\text{NH}_2 + \text{NO}_2$, which controls the nitrogen pool composition as well as the chain propagation in the system. In particular, the predicted N_2O concentration is sensitive to the branching fraction for this step. The N_2O profile is predicted almost quantitatively with the values of k_{1a} and k_{1b} recommended in the present work. For fixed values of β of 10 or 20%, predictions, though less accurate, are within experimental uncertainty. It is interesting to note that the experimental data support a branching fraction for $\text{NH}_2 + \text{NO}_2$ that decreases slightly with increasing temperature, in agreement with the theoretical results.

The chemistry involved, however, is quite complex and uncertainties in the rate constants for important side reactions preclude an accurate determination of k_1 or β from the flow reactor data. The NH_2 radical, formed mainly from $\text{NH}_3 + \text{OH}$, reacts largely with NO_2 ,

At temperatures below approximately 1100 K, the products of the $\text{NH}_2 + \text{NO}_2$ reaction, R1a and R1b, are fairly stable and both channels would in effect be considered chain terminating. The generation of chain carriers proceeds through reactions of the type $\text{H}_i\text{NO} + \text{NO}_2 \rightarrow \text{H}_{i-1}\text{NO} + \text{HONO}$, followed by dissociation of HONO ,¹³

There are no experimental data available on the $\text{HNO} + \text{NO}_2$ and $\text{H}_2\text{NO} + \text{NO}_2$ reactions, and the uncertainty in these rate constants imply that it is not possible from the data to determine independently the values of k_{1a} and k_{1b} . Above 1100 K, dissociations of H_2NO and HNO , respectively,

become competitive, and the system becomes less sensitive to the $\text{HNO} + \text{NO}_2$ and $\text{H}_2\text{NO} + \text{NO}_2$ reactions. A significant fraction of NO_2 is consumed by the fast step $\text{NO}_2 + \text{H} = \text{NO} + \text{OH}$, and the reaction $\text{NH}_2 + \text{NO} \rightarrow \text{products}$ assumes a more important role in consuming NH_2 . This last reaction is largely responsible for the increasing conversion of NH_3 and NO_2 to N_2 at higher temperatures.

CONCLUSIONS

The present combination of experiment, theory, and modeling provides a consistent picture for the effect of the $\text{NH}_2 + \text{NO}_2$

reaction on the SNCR process. The laser photolysis/LIF experiments yield a total rate constant of $k_{1,\text{exp}}(T) = 9.5 \times 10^{-7} (T/\text{K})^{-2.05} \exp(-404 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the 295–625 K regime. The present ab initio TST based master equation calculations yield a rate constant of $k_{1,\text{theory}}(T) = 7.5 \times 10^{-12} (T/\text{K})^{-0.172} \exp(687 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is in good agreement with the current experimental values. The theoretical analysis indicates that the two entrance channel adducts H_2NNO_2 and H_2NONO lead to formation of $\text{N}_2\text{O} + \text{H}_2\text{O}$ (R1a) and $\text{H}_2\text{NO} + \text{NO}$ (R1b), respectively. There is no indication of a rapid interconversion between the two adducts, although there is a roaming TS separating the two that introduces a very minor coupling of the two channels. The theoretical predictions tend to overestimate the branching ratio, defined as $\beta = k_{1a}/(k_{1a} + k_{1b})$, at lower temperatures, but this ratio is very sensitive to the details of the interaction potentials for the $\text{NH}_2 + \text{NO}_2$ addition channels. Modest adjustments of these interaction potentials yield values of $k_{1a} = 4.3 \times 10^{-6} (T/\text{K})^{-2.191} \exp(-229 \text{ K}/T)$ and $k_{1b} = 1.5 \times 10^{-12} (T/\text{K})^{0.032} \exp(761 \text{ K}/T)$. The corresponding branching ratio is then in good agreement with experiment over a wide range of temperature, and a model for the NH_3/NO_2 system then accurately reproduces the observed NO , NO_2 , and N_2O temperature-dependent concentration profiles. Thus, we recommend these rate coefficients for use in further modeling efforts.

ASSOCIATED CONTENT

Supporting Information

Extrapolations of measured rate constants to zero probe energy. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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