The Four Isotopomer Reactions of NH(a)and ND(a) with $NH_3(\tilde{X})$ and $ND_3(\tilde{X})$

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Dedicated to Prof. Dr. Klaus Scherzer on the occasion of his 70th birthday

(Received February 2, 2004; accepted February 13, 2004)

Kinetics / Isotope Effect / Laser-Induced Fluorescence / Complex-Forming Bimolecular Reaction

The reactions

$$\begin{split} & \mathsf{NH}(a) + \mathsf{NH}_3(\tilde{X}) \to \mathsf{products} & (1) \\ & \mathsf{ND}(a) + \mathsf{NH}_3(\tilde{X}) \to \mathsf{products} & (2) \\ & \mathsf{NH}(a) + \mathsf{ND}_3(\tilde{X}) \to \mathsf{products} & (3) \\ & \mathsf{ND}(a) + \mathsf{ND}_3(\tilde{X}) \to \mathsf{products} & (4) \end{split}$$

were studied in a quasi-static reaction cell at room temperature and pressures of 10 and 20 mbar with He as the main carrier gas. The electronically excited reactants NH(*a*) and ND(*a*) were generated by laser-flash photolysis of HN₃ and DN₃, respectively, at $\lambda = 308$ nm and detected by laser-induced fluorescence (LIF). Also the ground state species NH(*X*) and ND(*X*) as products were detected by LIF.

From the measured concentration-time profiles of NH(a) and ND(a) under pseudo-first order conditions, the following rate constants were obtained:

 $k_1 = (9.1 \pm 0.9) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ $k_2 = (9.6 \pm 1.0) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ $k_3 = (8.0 \pm 1.0) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ $k_4 = (7.2 \pm 0.8) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$

The major products are the corresponding $NH_iD_{2-i}(\tilde{X})$ radicals (i = 0, 1, 2), whereas quenching processes such as $NH(a) + ND_3 \rightarrow NH(X) + ND_3$ are of minor importance (1%). The isotope exchange $NH(a) + ND_3 \rightarrow ND(X) + NHD_2$ is negligible, and

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the corresponding channel on the singlet surface $NH(a) + ND_3(\tilde{X}) \rightarrow ND(a) + NHD_2(\tilde{X})$ contributes with 1% to the overall NH(a) depletion in that reaction. The experimental findings are discussed in terms of a chemical activation mechanism by means of statistical rate theory.

1. Introduction

The reactions of electronically excited singlet radicals like $NH(a \ \Delta)$ with molecules in their electronic ground state can be used to produce chemically activated complexes of well-known stable species in their electronic ground state, *e.g.* $CH_2(\tilde{a} \ A_1) + H_2O(\tilde{X} \ A_1) \rightarrow CH_3OH(\tilde{X} \ A_1)^*$ [1, 2]. Since in addition to the chemical energy from the newly formed bond, the electronic energy contributes to the internal excitation of the molecule, the method should be termed "electronic chemical activation". An interesting aspect of this method is that molecules with various amounts of vibrational energy can be generated by properly choosing the chemical nature and the electronic states of the reactants.

The reactions of NH($a^{1}\Delta$) with species containing hydrogen-element bonds generally proceed via insertion mechanisms [3]. Therefore, the reaction of NH($a^{1}\Delta$) with NH₃ can be used to produce vibrationally excited hydrazine, N₂H₄^{*}, in the electronic ground state. Its subsequent decomposition can be compared with that induced by other chemical activation processes such as H + N₂H₃ \rightarrow N₂H₄^{*} \rightarrow NH₂ + NH₂ [4]. For the overall reaction

$$\operatorname{NH}(a^{1}\Delta) + \operatorname{NH}_{3}(\tilde{X}) \to \operatorname{products}$$
 (1)

rate constants of 8.8×10^{13} cm³ mol⁻¹ s⁻¹ [5] and 6.6×10^{13} cm³ mol⁻¹ s⁻¹ [6] were determined at room temperature.

In contrast to NH($a^{1}\Delta$), the reaction of ground state NH($X^{3}\Sigma^{-}$) with ammonia is very slow with a rate constant $< 4.8 \times 10^{7} \text{ cm}^{3} \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K [7]. No indication for an insertion mechanism NH(X) + NH₃ \rightarrow N₂H₄ was found.

Many pyrolysis or photodissociation experiments with N₂H₄ have been performed [7–14]. In early studies by Wagner *et al.*, the decomposition of hydrazine behind reflected shock waves was investigated at temperatures between 1000 and 1600 K [12–14]. Besides the main dissociation channel N₂H₄ \rightarrow 2NH₂, also a possible contribution from the reaction N₂H₄ \rightarrow NH₃ + NH was discussed [14]. Therefore, it is interesting to look for NH(*X*) as a possible reaction product in our electronic chemical activation experiment.

The kinetics of reaction (1) can be compared with the kinetics of the reactions of ammonia with O(${}^{1}D$) and CH₂($\tilde{a} {}^{1}A_{1}$), which are isoelectronic to NH($a {}^{1}\Delta$).

For O(${}^{1}D$) + NH₃ rate constants of 3.8×10^{14} cm³ mol⁻¹ s⁻¹ [15] and 1.5×10^{14} cm³ mol⁻¹ s⁻¹ [16] are reported with no obvious temperature dependence in the range $204 \le T/K \le 354$ [16]. As reaction products, OH($X^{2}\Pi$) and NH(*a*) were detected, where the NH(*a*) concentration relative to that of OH(*X*)

is in the range 3%–15% [17]. A bimodal rotational distribution in OH(X, v = 0) found by Rettner *et al.* [18] is interpreted as being due to the simultaneous occurrence of an abstraction and an insertion channel.

The reaction of $CH_2(\tilde{a})$ with NH_3 proceeds in the temperature range $210 \le T/K \le 475$ with a rate constant of $1.7 \times 10^{14} (T/295 \text{ K})^{-1.2} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Because NH_2 radicals were detected as major products [19], an insertion mechanism was suggested [20].

In the present work, the four isotopomer reactions

$$\operatorname{NH}(a^{1}\Delta) + \operatorname{NH}_{3}(\tilde{X}) \to \operatorname{products}$$
 (1)

$$ND(a^{1}\Delta) + NH_{3}(X) \rightarrow products$$
 (2)

$$\operatorname{NH}(a^{1}\Delta) + \operatorname{ND}_{3}(\tilde{X}) \to \operatorname{products}$$
 (3)

 $ND(a^{1}\Delta) + ND_{3}(\tilde{X}) \rightarrow products$ (4)

are studied. Overall rate constants are determined and special emphasis is put on the possible isotope exchange pathways in reaction (2) and (3) on the singlet surface, *viz*.

$$ND(a^{1}\Delta) + NH_{3}(\tilde{X}) \to NH(a^{1}\Delta) + NDH_{2}(\tilde{X})$$
(2b)

$$\mathrm{NH}(a^{1}\Delta) + \mathrm{ND}_{3}(\tilde{X}) \to \mathrm{ND}(a^{1}\Delta) + \mathrm{NHD}_{2}(\tilde{X}).$$
(3b)

All active species, NH(*a*), NH(*X*), ND(*a*), ND(*X*), NH₂(\tilde{X}), NHD(\tilde{X}), and ND₂(\tilde{X}), can be directly observed by laser-induced fluorescence.

2. Experimental

The experiments were performed at room temperature in a quasistatic laserflash photolysis/laser-induced fluorescence (LIF) system, where "quasistatic" means that the flow through the reaction cell is negligible between the pump and the probe pulse but sufficient to exchange the gas volume between two subsequent pump pulses. The carrier gas was He at total pressures of 10 and 20 mbar.

The experimental set up is described in detail elsewhere [21], and only the essentials are repeated here. For the photolysis, a XeCl-exciplex laser (Lambda Physik LPX 205) with pulse energies in the range $200 \le E/\text{mJ} \le 400$ and a beam area of about 1.1 cm² was used. The probe laser was a dye laser (Lambda Physik FL 3002) with a fluence in the range $20 \le E/\text{mJ} \text{ cm}^{-2} \le 220$ and a beam area of 7 mm². It was pumped by an exciplex laser (Lambda Physik LPX205, XeCl; $230 \le E/\text{mJ} \le 290$). The fluence of the dye laser was shown to be sufficient to saturate the excited transition, and the frequency doubled laser beam with a fluence of $2 \le E/\text{mJ} \text{ cm}^{-2} \le 3$ was also sufficient to saturate the observed transition in OH (see below).

The NH(*a*) (ND(*a*)) radicals were produced by HN₃ (DN₃) photolysis in the $\tilde{A} - \tilde{X}$ band at $\lambda = 308$ nm with a rotational excitation significantly above room temperature. The rotationally hot population, however, relaxes to a thermal distribution mainly by collisions with He on a μ s time scale.

NH(*a*, v = 0) was detected by exciting the P₃ line at $\lambda = 326.22$ nm of the transition $c^{-1}\Pi$, $v' = 0 \leftarrow a^{-1}\Delta v'' = 0$, in the wavelength range $325 \leq \lambda/\text{nm} \leq 328$. The undispersed fluorescence from the excited state was observed perpendicular to the laser beam. ND(*a*, v = 0) was excited via the transition $c^{-1}\Pi$, $v' = 0 \leftarrow a^{-1}\Delta v'' = 0$ in the wavelength range $324 \leq \lambda/\text{nm} \leq 326$. For the kinetic measurements, the transition excited at $\lambda = 324.94$ nm (P₄-line) was used. We detected the undispersed fluorescence, using filters to suppress scattered radiation from the excitation beam.

For the detection of NH(*X*), the transition $A^{3}\Pi v' = 0 \leftarrow X^{3}\Sigma$, v'' = 0 was excited in the wavelength range $335.5 \le \lambda/\text{nm} \le 338.5$, and the fluorescence signal from the $A^{3}\Pi v' = 0$ state was recorded.

The NH₂(\tilde{X}^2B_1) radicals were detected by the fluorescence induced by the transition $\tilde{A}^2A_1(090) \leftarrow \tilde{X}^2B_1(000)$ at a wavelength of 597.65 nm.

Gases with the highest commercially available purity were used: He, 99.9999%, Praxair; NH₃, 99.998%, UCAR; D₂O, 99.8%, Merck and N₂, 99.995%, UCAR. HN₃ was synthesized by melting stearic acid, CH₃(CH₂)₁₆ COOH, with NaN₃. It was dried with CaCl₂ and stored in a bulb at partial pressures \leq 200 mbar diluted with He (overall pressure *ca*. 1 bar). For safety reasons, the HN₃ containing devices were covered with a wooden box since HN₃ is highly explosive even at low pressures.

The isotopomer DN₃ was obtained via the exchange reaction

$$HN_3 + D_2O \rightarrow DN_3 + HDO$$
 (5)

by adding D_2O to the storage bulb. Furthermore, it is to be noted that the reaction sequence

$$ND_3 + HN_3 \Leftrightarrow HD_3N_4 \Leftrightarrow NHD_2 + DN_3$$
 (6)

can also lead to isotope exchange.

3. Results and discussion

3.1 Reaction rates

The reactions (1)–(4) were studied under pseudo-first order conditions with ammonia in large excess over the imino radicals. The NH(*a*) radicals also react with the precursor molecules,

 $NH(a) + HN_3 \rightarrow products$

(7)

and, hence, the depletion of NH(a) has to be described by:

$$-d[NH(a)]/dt = k_i[NH(a)][R] + k_7[NH(a)][HN_3] + k_a[NH(a)][He]$$
(I)

with i = 1 and 3 and $[R] = [NH_3]$ and $[ND_3]$, respectively.

Because DN_3 is produced by reaction (5), the reactions of ND(a) with the different species occurring in this isotope exchange process have to be included into the rate law for the depletion of ND(a), *viz*.

 $ND(a) + HN_3 \rightarrow products$ (8)

 $ND(a) + DN_3 \rightarrow products$ (9) $ND(a) + D_2O \rightarrow products$ (10)

 $ND(a) + HDO \rightarrow products$ (11)

 $ND(a) + H_2O \rightarrow \text{products}$ (12)

It follows

$$- d[ND(a)]/dt = k_i[ND(a)][R] + k_8[ND(a)][HN_3] + k_9[ND(a)][DN_3] + k_{10}[ND(a)][D_2O] + k_{11}[ND(a)][HDO] + k_{12}[ND(a)][H_2O]$$
(II)
+ k_q[ND(a)][He]

with i = 2 and 4 and $[R] = [NH_3]$ and $[ND_3]$, respectively.

Since all terms in Eqn. (I) and (II) are first-order with respect to the imino radical, they can be combined to give

 $-d[NH(a)]/dt = k_{eff}^{I}[NH(a)]$

and

 $-d[ND(a)]/dt = k_{eff}^{II}[ND(a)].$

In general, the physical quenching by He can be neglected, because $k_q < 6 \times 10^8$ cm³ mol⁻¹ s⁻¹ [22]. The relevant concentrations of the other species, HN₃, DN₃, D₂O, HDO and H₂O, are given in the headings of Tables 1–4. In the case of reaction (2) (Table 2), it was assumed that [DN₃] is nearly equal to [HN₃] in presence of an excess of D₂O due to the isotope exchange reaction (5). This assumption, which is not essential for the determination of the rate constants, is supported by the observation of nearly equal NH(*a*)/ND(*a*) fluorescence signal intensities. In Table 4, the sum of the concentrations of D₂O and HDO is given. The formation of H₂O due to the secondary reaction

$$HDO + HN_3 \rightarrow H_2O + DN_3 \tag{13}$$

was neglected since it does not influence the resulting rate constants significantly. The consumption of NH(a) and ND(a), respectively, in the absence of

T K	P mbar	time range μs	$[NH_3]$ 10 ⁻⁹ mol cm ⁻³	$\frac{k_{\rm eff}^{\rm I}}{10^5~{\rm s}^{-1}}$	$k_1^{\rm I}$ $10^5 { m s}^{-1}$
293	10.1	0-200	0	0.027	0
293	10.0	0 - 80	0.3	0.35	0.32
293	9.9	0-34	0.7	0.69	0.66
293	10.0	0-18	1.4	1.29	1.26
293	10.0	0-11	2.1	1.87	1.84
293	9.9	0-8	2.8	2.68	2.65
293	9.9	0-7	3.6	3.23	3.20

Table 1. Experimental results for reaction (1), $NH(a) + NH_3 \rightarrow products$, $[HN_3] = 3.4 \times 10^{-11} \text{ mol cm}^{-3}$.



Fig. 1. Semilogarithmic plot of [ND(a)] as a function of reaction time (t_R) for reaction (2); NH₃ concentration (in 10^{-9} mol cm⁻³): $\blacktriangle = 0.0, \ \varPhi = 0.3, \ \bigcirc = 0.7, \ \blacksquare = 2.1, \ \square = 3.6.$

 NH_3 and ND_3 was measured in independent experimental runs, and the results are also included in Tables 1–4. We note that the upper limit of the NH_3 concentration is determined by the equilibrium $HN_3 + NH_3 \Leftrightarrow NH_4N_3(s)$ since the formation of solid NH_4N_3 is to be avoided.

Reaction (1) was studied at a pressure of 10 mbar under pseudo first-order conditions in the range $1.6 \leq [NH_3]_0/([NH(a)]_0 \times 10^4) \leq 20$, and the results are given in Table 1. The depletion of NH(*a*) solely by the precursor molecule HN₃ was measured in independent experiments ([NH₃]₀ = 0). They lead to a pseudo-first order rate constant k_7 [HN₃] = $2.7 \times 10^3 \text{ s}^{-1}$, which corresponds

T	P	time range	$[NH_3]$	$k_{ m eff}^{ m II}$	$k_2^{\rm II}$
K	mbar	μs	10 ⁻⁹ mol cm ⁻³	$10^5~{ m s}^{-1}$	$10^5 { m s}^{-1}$
293 293 293 293 293 293 293 293	10.0 10.0 10.1 10.1 10.1 9.9 10.0	0-200 0-80 0-34 0-18 0-11 0-8 0-7	0 0.3 0.7 1.4 2.1 2.8 3.6	0.026 0.38 0.72 1.45 2.02 2.73 3.46	0 0.35 0.69 1.42 1.99 2.70 3.43

Table 2. Experimental results for reaction (2), $ND(a) + NH_3 \rightarrow \text{products}$, $[DN_3] \approx [HN_3] \approx 1 \times 10^{-11} \text{ mol cm}^{-3}$, $[D_2O] + [HDO] \approx 4 \times 10^{-11} \text{ mol cm}^{-3}$.

to $k_7 = 7.9 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in good agreement with the value of $7.3 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ reported in Ref. [23]. Consequently, $k_7[\text{HN}_3]$ is subtracted from all values for $k_{\text{eff}}^{\text{I}}$ in order to obtain $k_1[\text{NH}_3]$. A plot of $k_1^{\text{I}} = k_{\text{eff}}^{\text{I}} - k_7[\text{HN}_3]$ versus [NH₃] leads to a straight line through the origin, and the slope provides the second-order rate constant:

$$k_1 = (9.1 \pm 0.9) \times 10^{13} \,\mathrm{cm}^3 \,\mathrm{mol}^{-1} \,\mathrm{s}^{-1}$$

which is in good agreement with a value of $8.8 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ determined earlier in our laboratory [5]. The determination of the rate constant k_1 was repeated in the present work in order to allow for a direct comparison with the other isotopomer reactions.

Reaction (2) was studied under pseudo-first order conditions in the range $1.6 \leq [NH_3]_0/([ND(a)]_0 \times 10^3) \leq 20$. The rate constant k_{eff}^{II} follows from a plot of log $([ND]/[ND]_0)$ vs. time as displayed in Fig. 1. The nearly horizontal line for $[NH_3] = 0$ corresponding to a rate constant of $k_{eff}^{II} = 2.6 \times 10^3 \text{ s}^{-1}$ demonstrates that reactions with molecules other than NH₃ contribute with less than 10% to the overall rate of depletion of ND(*a*) (*cf*. Table 2). The plot of $k_2^{II} = k_{eff}^{II} - 2.6 \times 10^3 \text{ s}^{-1}$ versus $[NH_3]$ leads to a straight line through the origin, the slope of which provides the second-order rate constant:

$$k_2 = (9.6 \pm 1) \times 10^{13} \,\mathrm{cm}^3 \,\mathrm{mol}^{-1} \,\mathrm{s}^{-1}$$
.

The results for reaction (3) are summarized in Table 3. A rate constant $k_{\text{eff}}^{\text{I}} = 3.2 \times 10^3 \text{ s}^{-1}$ is obtained in absence of ND₃, which can be again essentially attributed to the reaction of NH(*a*) with HN₃. The rate constant $k_{\text{eff}}^{\text{I}}$ is determined in a completely analogous manner to that for reaction (1). From the slope of a plot of $k_3^{\text{I}} = k_{\text{eff}}^{\text{I}} - 3.2 \times 10^3 \text{ s}^{-1} \text{ vs.}$ [ND₃], a second order rate constant

$$k_3 = (8.0 \pm 1.0) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

T	P	time range	$[NH_3]$	$k_{ m eff}^{ m I}$	k_3^{I}
K	mbar	µs	10 ⁻⁹ mol cm ⁻³	$10^5~{ m s}^{-1}$	10 ⁵ s ⁻¹
293 293 293 293 293 293 293 293	10.0 10.0 10.1 10.1 10.1 10.0 10.1	$\begin{array}{c} 0-200\\ 0-80\\ 0-34\\ 0-18\\ 0-11\\ 0-8\\ 0-8\end{array}$	0 0.3 0.7 1.4 2.1 2.8 3.6	0.032 0.32 0.70 1.18 1.64 2.30 2.96	0 0.29 0.67 1.15 1.61 2.27 2.93
293	10.1	0-7	4.1	3.31	3.28
293	10.1	0-7	8.1	6.47	6.44

Table 3. Experimental results for reaction (3), $NH(a) + ND_3 \rightarrow products$, $[HN_3] = 4.4 \times 10^{-11} \text{ mol cm}^{-3}$.

Table 4. Experimental results for reaction (4), $ND(a) + ND_3 \rightarrow products$, $[DN_3] \approx [HN_3] \approx 1 \times 10^{-11} \text{ mol cm}^{-3}$, $[D_2O] + [HDO] \approx 4 \times 10^{-11} \text{ mol cm}^{-3}$.

T	P	time range	$[NH_3]$	$k_{\rm eff}^{\rm II}$	$k_4^{ m II} \ 10^5 { m s}^{-1}$
K	mbar	µs	10 ⁻⁹ mol cm ⁻³	10 ⁵ s ⁻¹	
293 293 293 293 293 293 293 293 293 293	10.0 10.0 10.1 10.1 10.1 10.1 10.1 10.1	$\begin{array}{c} 0-200\\ 0-80\\ 0-34\\ 0-18\\ 0-11\\ 0-10\\ 0-10\\ 0-10\\ 0-8\\ 0-8\\ 0-8\\ 0-8\end{array}$	0 0.3 0.7 1.4 2.1 2.8 3.6 4.1 6.0 8.1	0.03 0.31 0.63 1.07 1.66 2.39 2.56 2.93 4.33 5.80 8.70	0 0.28 0.60 1.04 1.63 2.36 2.53 2.90 4.30 5.77

was obtained, *i.e.* the reaction of NH(a) with ND_3 is somewhat slower than the reaction with NH_3 .

The results for reaction (4) are contained in Table 4. The pseudo-first order plots are shown in Fig. 2, and the rate constant k_4 follows from a plot of $k_4^{II} = k_{eff}^{II} - 3.0 \times 10^3 \text{ s}^{-1} \text{ vs. [ND_3]}$ as described above. We obtained

 $k_4 = (7.2 \pm 0.8) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

which is the lowest value of all isotopomer reactions. Obviously, ND_3 reacts slower than NH_3 whereas ND(a) and NH(a) react with similar rates.



Fig. 2. Semilogarithmic plot of [ND(a)] as a function of reaction time (t_R) for reaction (4); ND₃ concentrations (in $10^{-9} \text{ mol cm}^{-3}$): $\bullet = 0.3$; $\circ = 0.7$; $\blacksquare = 1.4$; $\square = 2.1$, $\blacktriangle = 4.1$.

3.2 Reaction products

The main product channel for reaction (1) is:

$$\operatorname{NH}(a) + \operatorname{NH}_3(\tilde{X}) \to 2\operatorname{NH}_2(\tilde{X})$$
 (1a)

with $k_{1a}/k_1 = 0.93$ [5], and the analogous reaction pathways were found to be dominant for all four isotopomer reactions.

Additionally, there are exchange-reaction pathways on the singlet surface conceivable, which are detectable for reaction (2) and (3), *viz*.

$$ND(a) + NH_3 \rightarrow NH(a) + NH_2D$$
 (2b)

$$NH(a) + ND_3 \rightarrow ND(a) + NHD_2$$
. (3b)

In the present work, we restrict our investigations on reaction (3b), since NH(a) can be directly generated from HN_3 whereas ND(a) is obtained from DN_3 , which has to be produced in the preceding isotope exchange reaction (5).

The measured concentration-time profile for ND(*a*) as a product of reaction (3) is shown in Fig. 3. The finite concentration of ND(*a*) at $t_{\rm R} = 0$ is caused by the isotope exchange reaction

$$ND_3 + HN_3 \Leftrightarrow HD_3N_4 \Leftrightarrow NHD_2 + DN_3$$
(6)

which already occurs in the mixing region of our experimental setup. The photolysis of DN_3 then leads to the observed $[ND(a)]_0 \neq 0$. The shortest mixing



Fig. 3. The ND(*a*) fluorescence intensity *vs.* reaction time for reaction (3) with $[ND_3] = 4.1 \times 10^{-10} \text{ mol cm}^{-3}$, $[HN_3] = 5 \times 10^{-10} \text{ mol cm}^{-3}$, $[ND(a)]_0 = 2 \times 10^{-15} \text{ mol cm}^{-3}$, $[NH(a)]_0 = 5 \times 10^{-13} \text{ mol cm}^{-3}$, $[ND_3] = 4.1 \times 10^{-10} \text{ mol cm}^{-3}$, mixing time $t \approx 1 \text{ ms}$, • experimental results; simulations of the reaction system with: ---- $k_{3b} = 1.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $-k_{3b} = 8 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $\cdots k_{3b} = 4 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

time led to a ratio of the initial concentrations $[ND(a)]_0/[NH(a)]_0 \approx 0.01$. It can be seen from Fig. 3 that there is an increase of [ND(a)] for small reaction times, which is interpreted as a formation of ND(a) in a chemical reaction. From the concentration-time profile in Fig. 3, a rate constant for reaction (3b) was estimated by a simulation of a complex reaction mechanism consisting of reactions (1), (2), (3), (3b), and (4), where only the rate constant k_{3b} was treated as a parameter (*cf.* Fig. 3).

The initial concentration $[ND(a)]_0$ was estimated to be 2×10^{-15} mol cm⁻³, and it was found in the simulation that the [ND(a)] profile is not very sensitive to this initial concentration. The interpretation of the ND(*a*) concentrationtime profiles is not simple due to the small ND(*a*) concentrations and the low signal to noise ratio. The measured concentration profiles can be interpreted with a rate constant $k_{3b} \approx 8 \times 10^{11}$ cm³ mol⁻¹ s⁻¹, and, thus, it can be estimated that about 1% or less of the reaction proceeds via the exchange channel (3b).

This reaction pathway is endoergic with $\Delta E_{zp} = 2.6 \text{ kJ/mol}$ (zero-point energies from HF/6-31G* frequencies scaled by 0.89, see below), and from an energetic point of view, it would be more favourable to study the reaction (2b). However, there was no way to get DN₃ sufficiently pure. For reaction (2), in which the isotope exchange reaction pathway is exoergic by -2.3 kJ/mol, one could expect a contribution of about 3% to the overall depletion of NH(*a*) via reaction (2b). From these results it can be concluded that the NH(*a*) forma-

tion is of minor importance in the N_2H_4 decomposition even at high excitation energies.

The quenching channel

$$NH(a) + NH_3 \rightarrow NH(X) + NH_3$$
 (1c)

has been investigated by comparing [NH(X)] from reaction (1) with $[NH(X)]_{N_2}$, the NH(X) concentration in the reaction

$$\mathrm{NH}(a) + \mathrm{N}_2 \to \mathrm{NH}(X) + \mathrm{N}_2 \,. \tag{14}$$

In the absence of NH₃ and in a large excess of N₂ over HN₃, all NH(*a*) initially present is converted to NH(*X*) at long reaction times, *i.e.*, $[NH(a)]_0 = [NH(X)]_{N_2\infty}$. The consumption of NH(*X*) under these experimental conditions can be neglected as seen from the NH(*X*) profiles. In the absence of N₂, the NH(*X*) radicals are formed in reaction (1c) since quenching by other species in the system (HN₃, He) is unimportant. The NH(*X*) consumption can again be neglected. Thus, the fraction k_{1c}/k_1 can be determined directly from the ratio

$$\frac{k_{1c}}{k_1} = \frac{[\operatorname{NH}(X)]_{\infty}}{[\operatorname{NH}(a)]_0} = \frac{[\operatorname{NH}(X)]_{\infty}}{[\operatorname{NH}(X)]_{N_2\infty}}$$

where $[NH(X)]_{\infty}$ and $[NH(X)]_{N_{2}\infty}$ are the NH(X) concentrations at long reaction times due to reaction (1c) and (14), respectively. The reaction

$$NH(a) + HN_3 \rightarrow NH(X) + HN_3$$
 (7c)

leads to a small correction which could be neglected.

It turns out that reaction (1c) is of minor importance, and

$$k_{1c}/k_1 = 0.006 \pm 0.003$$
.

From an analogous analysis of [ND(X)], it follows that this is true for the isotopomer reactions

$$ND(a) + NH_3 \rightarrow ND(X) + NH_3$$
 (2c)

and

$$ND(a) + ND_3 \rightarrow ND(X) + ND_3$$
. (4c)

The contributions of the quenching channel were too small to detect an exchange reaction pathway as e.g.,

$$NH(a) + ND_3 \rightarrow ND(X) + NHD_2$$
 (15)

due to the ND(*a*) being present in the system (see above).



Fig. 4. Schematic energy diagram of the lowest singlet surface of N_2H_4 and steady-state population f(E) of HN–NH₃.

3.3 Modeling by statistical rate theory

There are several theoretical studies dealing with the structure and energetics of the intermediates occurring in the $NH(a) + NH_3$ reaction [24–27]. However, there is only one work, where also kinetic quantities are estimated [28]. Hence, in order to characterize the reaction mechanism and to verify the rate constants and the isotope effect, we perform in the following an analysis using RRKM [29–32] and SACM [31–35] calculations.

The basic mechanism was proposed by Pople *et al.* [24] and essentially confirmed by two more recent studies [25, 26]. It is assumed that NH(a) and NH_3 at first form an adduct, $HN-NH_3$, which subsequently isomerizes to H_2N-NH_2 . Then, H_2N-NH_2 can dissociate into $NH_2 + NH_2$:

$$NH(a) + NH_3 \Leftrightarrow HN - NH_3$$
 (A)

$$HN-NH_3 \Leftrightarrow H_2N-NH_2 \tag{B}$$

$$\mathrm{H}_{2}\mathrm{N}-\mathrm{N}\mathrm{H}_{2} \to \mathrm{H}_{2}\mathrm{N}+\mathrm{N}\mathrm{H}_{2}\,. \tag{C}$$

Because the following considerations are independent of the specific isotopic substitution, these unimolecular steps are denoted here in a general way as (A), (B) and (C).

A schematic energy diagram for this reaction sequence is shown in Fig. 4, and the relative energies used in this work are compiled in Table 5. They are based on the following heats of formation (in kJ mol⁻¹) [36]: NH(*a*), 502 (term energy from Ref. [37]); NH₃, -45.9; H₂N–NH₂, 95.4; NH₂, 185. For the adduct HN–NH₃ and TS_B, the transition state of reaction step (B), we adopted

Table 5. Energies relative to H_2N-NH_2 ; in parentheses values for the deuterated species relative to D_2N-ND_2 ; $\langle E \rangle_f$ represents the average energy of the intermediate population for T = 300 K.

	$E_{\rm rel}/{\rm kJmol^{-1}}$
$\begin{array}{l} \mathrm{NH}(a) + \mathrm{NH}_{3} \\ \mathrm{HN}{-}\mathrm{NH}_{3} \\ \mathrm{TS}_{\mathrm{B}} \\ \mathrm{NH}_{2} + \mathrm{NH}_{2} \\ \mathrm{H}_{2}\mathrm{N}{-}\mathrm{NH}_{2} \\ \langle E \rangle_{f} \end{array}$	361 (367) 182 (182) 281 (285) 274 (282) 0 (0) 366 (373)

the *ab initio* results from Skurski *et al.* [27] (MP2/aug-cc-p VDZ + diffuse *s*, *p*, *d*, (*f*) functions).

It becomes evident that, due to the exoergicity of reaction steps (A) and (B), HN–NH₃ as well as H_2N –NH₂ are ro-vibrationally excited, and the kinetics of the system has to be described by the rate constants for electronic chemical activation conditions. Because of the low pressures in our experiments, the unimolecular reactions of the excited intermediates turn out to be much faster than the collisional deactivation (see below). Therefore, the steady-state populations of the intermediates can be approximated by the distribution function [30–32]

$$f(E) = \frac{W(E) \exp(E - /k_{\rm B}T)}{\int\limits_{0}^{\infty} W(\varepsilon) \exp(-\varepsilon/k_{\rm B}T)} d\varepsilon$$
(III)

where W is the sum of states of HN–NH₃, k_B is Boltzmann's constant, and T denotes the temperature. The rate constants for the unimolecular steps i = (-a), (B), (-B) and (C) follow by averaging:

$$k_i = \int_0^\infty k_i(E) f(E) dE$$
 (IV)

where the specific rate constants $k_i(E)$ are calculated by statistical models [30–32] according to:

$$k_i(E) = \frac{W_i(E - E_{0i})}{\hbar\rho(E)}.$$
(V)

Here, $\rho(E)$ is the density of states of the respective reactant, HN–NH₃ or H₂N–NH₂, and \hbar denotes Planck's constant. The number of open reaction channels W_i is calculated for reactions steps i = (-A) and (C) by the simplified Statistical Adiabatic Channel Model [35] and is identified for reaction steps (B) and (-B) with the sum of states of the transition state according to the RRKM model [29]; E_{0i} is the corresponding threshold energy.

Reaction step	Н	D
(A)	9.1×10^{13} *	8.4×10^{13}
(-A)	1.8×10^{9}	$7.0 imes 10^8$
(B)	6.0×10^{11}	$3.0 imes 10^{11}$
(- B)	9.4×10^{9}	3.7×10^{9}
(C)	1.2×10^{12}	6.1×10^{11}
(- C)	$4.8 \times 10^{13}^{*}$	$4.5 imes 10^{13}$

Table 6. Rate constants for the unimolecular steps (s^{-1}) from Eqn. (IV) <u>and</u> bimolecular rate constants $(cm^3 mol^{-1} s^{-1})$ from canonical SACM.

* adjust, see text.

All sums and densities of states were exactly counted [35, 38] for a total angular momentum quantum number J = 20, which is essentially governed by the orbital momentum caused by the capture process NH(*a*) + NH₃ [39]. The molecular properties required were taken from the following sources: NH(*a*) [37]; ND(*a*), calculated from the NH data by exchanging H for D; NH₃ and ND₃ [40]; NH₂ and ND₂ [41]; HN–NH₃, TS_B and H₂N–NH₂ as well as their deuterated isotopomers, calculated *ab initio* on HF/6-31G*-level [42] (frequencies scaled by 0.89 [43]).

The high-pressure limiting value of the bimolecular rate constant for NH(*a*) + NH₃ was computed by the canonical version of the simplified SACM [34], where the anisotropy parameter α/β [44] was adjusted so as to reproduce our measured rate constant of $k_1 = 9.1 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ($\alpha/\beta = 0.493$). As isotopic substitution does not alter the anisotropy of the interfragment potential, the same value for α/β has been used in the calculation for ND(*a*) + ND₃, and a rate constant of $k_4 = 8.4 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was obtained. It is to be noted that the predicted ratio of $k(\text{NH}(a) + \text{NH}_3)/k(\text{ND}(a) + \text{ND}_3) = 1.1$ is somewhat below the experimental value of 1.3; nevertheless, the isotope effect is reproduced in the calculations of the specific rate constants for the reaction step (-A) by the microcanonical version of SACM.

In an analogous approach, the specific rate constants for the reaction step (C) were calculated. Here, a value of $\alpha/\beta = 0.65$ was used; it was obtained from an adjustment of the recombination rate constant for NH₂ + NH₂ to an average experimental value of $\sim 5 \times 10^{13}$ cm³ mol⁻¹ s⁻¹ [45]. Because the available experimental data exhibit a considerable scatter [45], the results for $k_{\rm C}(E)$ are rather uncertain. As, however, they exceed $k_{\rm -B}(E)$ by at least two orders of magnitude, this has no influence on the overall kinetics. The resulting rate constants for the steps (A)–(C) and their reverse reactions are summarized in Table 6.

4. Conclusions

From the analysis of our experimental results on the isotopomer reactions of NH(a) and ND(a) with $NH_3(\tilde{X})$ and $ND_3(\tilde{X})$ in terms of statistical rate theory, the following conclusions can be drawn:

- 1. the measured bimolecular rate coefficients represent high-pressure limiting (or capture) values, because back dissociation (-A) is at least two orders of magnitude slower than isomerization (B) to hydrazine,
- hydrazine, once formed, essentially dissociates into NH₂ + NH₂ via reaction step (C); back isomerization (-B) is again two orders of magnitude slower,
- 3. the vanishing contribution of the isotope-exchange channels for the partially deuterated species becomes evident in this way,
- 4. the lifetimes of HN–NH₃ and H₂N–NH₂ formed from NH(*a*) + NH₃ are in the picosecond range; collision numbers $> 10^{12} \text{ s}^{-1}$ are required for a stabilization of the intermediates,
- 5. the overall kinetics is not influenced by isotopic substitution; the isotope effect observed is due to the isotope dependence of the capture rate, it can be reproduced by canonical SACM calculations,
- 6. our experimental results are compatible with the reaction route (A)–(C).

Acknowledgement

Thanks are due to the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 357 "Molekulare Mechanismen unimolekularer Prozesse") and the Fonds der Chemischen Industrie for financial support.

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