# A High-Temperature Photochemistry Study of the D + ND<sub>3</sub> Reaction

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The kinetics of the  $D + ND_3$  reaction (2) has been studied from 590 to 1220 K by using the high-temperature photochemistry (HTP) technique. D(12S) atoms were generated by flash photolysis of ND3 and monitored by time-resolved atomic resonance fluorescence with pulse counting.  $k_2(T)$  is determined to be  $3.2 \times 10^{-10} \exp(-8810 \text{ K/T}) \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>. Accuracy assessments are discussed in the text. Comparison to  $k_1(T)$  for H + NH<sub>3</sub> (1) measured in the same apparatus and over a similar temperature range shows that  $k_2(T)$  is smaller.  $k_1(T)$  and  $k_2(T)$  agree reasonably well with calculations based on transition-state theory and a simple tunneling model using the same potential energy surface for both reactions. Considered alone,  $k_2(T)$  can also be modeled without tunneling.

### Introduction

The dependence of the rate coefficient for the reaction

$$H + NH_3 \rightarrow H_2 + NH_2 \tag{1}$$

on temperature has recently been investigated by using three different techniques for studying isolated elementary reactions: high-temperature photochemistry (HTP) from 500 to 1140 K,<sup>1</sup> flash photolysis/shock tube (FP-ST) from 910 to 1780 K,<sup>2</sup> and discharge flow (DF) from 670 to 1000 K.<sup>3</sup> The results are in good agreement and showed that earlier measurements gave rate coefficients that were too low. As a comparison, we have now carried out kinetic measurements from 590 to 1220 K on the deuterium analogue reaction

$$D + ND_3 \rightarrow D_2 + ND_2 \tag{2}$$

for which no previous experimental data are available.

## **Experimental Section**

The HTP rate coefficient measurements for reaction 2 were made essentially as described in our earlier work on reaction 1.1 ND<sub>3</sub> (Cambridge Isotope Laboratories, 99.5% isotopic purity) was injected through a movable cooled inlet into the reactor and heated without heterogeneous decomposition by mixing with much larger quantities of heated Ar bath gas.<sup>1,4</sup> D atoms were generated in the effectively wall-less reaction zone by flash photolysis through a magnesium fluoride window.<sup>1</sup> Their subsequent loss through reaction with ND<sub>3</sub> and diffusion was monitored by time-resolved atomic resonance fluorescence with pulse counting and signal averaging. The source of resonance radiation at  $\lambda = 121.5$  nm  $[D(2^2P) \rightarrow D(1^2S)]$  was a microwave discharge through about 1.5 Torr of 1%  $D_2$  in He. The fluorescence signal was spectrally isolated by a dry air filter in front of the photomultiplier tube.<sup>1</sup>

Under the pseudo-first-order conditions which apply in the HTP reactor,  $[D] \ll [ND_3]$ , the fluorescence intensity  $I_t$  is given by

$$I_{t} = I_{0} \exp(-k_{ps1}t) + B$$
(3)

 $I_0$  is the initial intensity, B is a steady background from scattered light, and

$$k_{\rm ps1} = k_{\rm DIFF} + k_2[\rm ND_3] \tag{4}$$

where  $k_{\text{DIFF}}$  represents essentially diffusional loss.<sup>1,4</sup> Decays of the form of eq 3 were captured and analyzed by using a threeparameter, nonlinear least-squares routine.<sup>5</sup>  $k_2$  was obtained from the slopes of plots of  $k_{ps1}$  versus [ND<sub>3</sub>]. The method for error analysis yielding  $\sigma_T$  and  $\sigma_{k2}$  is the same as used before.<sup>1</sup>

#### Results

Table I lists 25 determinations of  $k_2$  from 590 to 1220 K, together with the experimental parameters P, [M],  $\bar{v}$ , l, and F. These represent the pressure, total concentration, average linear gas velocity, distance from the movable cooled inlet to the reaction zone, and energy dissipated in the flash lamp, respectively. The  $k_2$  data are found to be independent of variation in [M], by a factor of 8,  $\vec{v}$  by a factor of 11, l by a factor of 4, and F by a factor of 5. This shows that the gas flows were well-mixed and attained thermal equilibrium, that no significant thermal decomposition of  $ND_3$  occurred, and that there were no kinetic complications from processes involving photolysis or reaction products.<sup>1,4</sup>

The  $k_2$  values obtained range from approximately  $1 \times 10^{-16}$  at 590 K to  $2 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 1220 K. The lower temperature limit is set by the large [ND<sub>3</sub>] (which absorbs resonance radiation) required for significant changes in  $k_{ps1}$  (eq 4): the large reaction tube diameter of 5 cm gives a low  $k_{\rm DIFF}$  so that small changes in  $k_{ps1}$  can be observed. At this limit  $k_{ps1}$  values from about 1 to 1.5 times  $k_{DIFF}$  were measured, a range which increased at higher temperatures. Typical  $k_{DIFF}$  values fell in the range 20-100 s<sup>-1</sup>. The larger values correspond to the lower pressures and higher temperatures of Table I. The upper temperature limit for  $k_2$  measurements comes from the fastest decays that can conveniently be monitored in the presence of sufficient  $ND_3$  to give a good  $\bar{D}$  atom yield and fluorescence signal.

Figure 1 shows the  $k_2$  results plotted in Arrhenius form. They may be fitted to the simple expression  $A \exp(-B \text{ K}/T) \text{ cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup> to yield

## $k_2(T) = 3.2 \times 10^{-10} \exp(-8810 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (5)

The line defined by eq 5 is drawn in Figure 1. The variances<sup>6</sup> of the parameters A and B are  $\sigma_A^2 = 1.3 \times 10^{-20}$  and  $\sigma_B^2 = 9.2$  $\times$  10<sup>4</sup>. Coupling between the parameters is reflected by the covariance<sup>7</sup>  $\sigma_{AB} = 3.4 \times 10^{-8}$ . We use the variances and the covariance to estimate  $2\sigma$  statistical confidence intervals for  $k_2(T)$ . Comparison of the three recent determinations of  $k_1(T)$  indicates the possibility of systematic differences of around  $\pm 15\%$  for these pieces of work.<sup>1-3</sup> We believe systematic errors to be absent from our HTP experiments yet allow for similar but unrecognized systematic uncertainty here to arrive at overall  $2\sigma$  confidence intervals for  $k_2(T)$ . These are about ±40% at 590 K, ±30% at 650 K,  $\pm 20\%$  at 900 K, and  $\pm 30\%$  at 1220 K.

#### Discussion

Figure 1 also shows our earlier data for  $k_1$  obtained in the same HTP reactor,<sup>1</sup> which can be compared directly to the present results. It may be seen that at all temperatures  $k_2(T)$  is smaller

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TABLE I: Summary of Rate Coefficient Measurements on D + ND<sub>3</sub>

$T \pm \sigma_T, K$	P, <sup>a</sup> Torr	$[M], 10^{18} \text{ cm}^{-3}$	$[ND_3], 10^{16} \text{ cm}^{-3}$	$\bar{v}$ , cm s <sup>-1</sup>	l, cm	<i>F</i> , J	$k \pm \sigma_k$ , cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
591 ± 12	330	5.5	0.9-14.3	4.7	15	42	$1.2 \pm 0.1 \ (-16)^b$
$617 \pm 12$	260	4.0	0.49-6.10	11	12	14	$2.6 \pm 0.3 (-16)$
$646 \pm 13$	420	6.3	0.7-10.9	6.0	12	9	$2.6 \pm 0.2 (-16)$
$654 \pm 13$	280	4.1	0.12-2.05	6.3	6	42	$6.4 \pm 0.7 (-16)$
666 ± 13	330	4.7	1.3-10.9	4.4	8	27	$4.6 \pm 1.1 \ (-16)$
$682 \pm 14$	270	3.8	0.17-2.15	5.6	14	42	$1.1 \pm 0.1 (-15)$
$717 \pm 14$	290	3.9	0.15-1.97	6.5	15	42	$1.6 \pm 0.1 (-15)$
$718 \pm 14$	460	6.1	0.32-2.97	3.6	8	14	$8.9 \pm 0.6 (-16)$
$761 \pm 15$	270	3.4	0.12-1.91	6.3	14	42	$3.3 \pm 0.1 (-15)$
$788 \pm 16$	250	3.1	0.10-1.01	12	14	42	$4.2 \pm 0.5 (-15)$
791 ± 16	170	2.1	0.21-2.29	14	21	14	$4.1 \pm 0.5 (-15)$
$792 \pm 16$	420	5.2	0.16-2.64	4.9	6	42	$2.9 \pm 0.2 (-15)$
$817 \pm 16$	500	5.9	0.09-2.00	6.3	4	14	$3.7 \pm 0.2 (-15)$
$823 \pm 16$	64	0.75	0.08-0.37	34	6	42	$1.3 \pm 0.1 (-14)$
$849 \pm 17$	160	1.8	0.28-1.92	21	12	14	$9.0 \pm 0.5 (-15)$
$882 \pm 18$	310	3.3	0.11-1.15	11	4	17	$9.7 \pm 0.4 (-15)$
$885 \pm 18$	120	1.3	0.09-0.63	20	6	42	$1.7 \pm 0.2 (-14)$
$927 \pm 19$	240	2.5	0.05-0.35	15	14	42	$3.8 \pm 0.3 (-14)$
955 ± 19	170	1.7	0.05-0.59	22	12	17	$2.8 \pm 0.4 (-14)$
$998 \pm 20$	310	3.0	0.05-0.28	12	14	42	$6.3 \pm 0.8 (-14)$
$1051 \pm 21$	360	3.3	0.03-0.43	28	4	28	$4.7 \pm 0.4 (-14)$
$1102 \pm 22$	210	1.8	0.05-0.23	20	6	42	$1.2 \pm 0.1 (-13)$
$1123 \pm 22$	140	1.2	0.02-0.13	31	6	42	$1.9 \pm 0.3 (-13)$
$1209 \pm 24$	240	1.9	0.05-0.26	47	4	42	$2.0 \pm 0.4 (-13)$
$1215 \pm 24$	270	2.1	0.07-0.28	17	6	42	$2.2 \pm 0.3 (-13)$

<sup>a</sup> 1 Torr = 133.3 Pa. <sup>b</sup>Should be read as  $(1.2 \pm 0.1) \times 10^{-16}$ .



Figure 1. Summary of the rate coefficients obtained for the reaction D  $+ ND_3 \rightarrow D_2 + ND_2$ , and comparisons (i) with rate coefficients for the reaction  $H + NH_3 \rightarrow H_2 + NH_2$  obtained in the same HTP apparatus and (ii) with theory (see text): (+) D + ND\_3, experimental data, present work (error bars represent  $\pm \sigma_T$  and  $\pm \sigma_k$ ); (O) H + NH<sub>3</sub>, experimental data from ref 1 (error bars are similar to those for D + ND<sub>3</sub> but are not shown here for clarity); (-) best fit to D + ND<sub>3</sub> data; (...) theoretical estimate for D + ND<sub>3</sub>; (---) theoretical estimate for H + NH<sub>3</sub>.

than  $k_1(T)$ . We shall show that essentially the same potential surface and analysis method earlier applied to reaction  $1^{1,2}$  leads, without adjustment to force a fit to  $k_2$ , to good agreement with both the  $k_1(T)$  and  $k_2(T)$  data. We therefore begin by establishing transition-state theory (TST) parameters for the H + NH<sub>3</sub> system,<sup>8,9</sup> and then in order to calculate  $k_2$  make changes based solely

TABLE II: BAC-MP4 Results for the Reactions H + NH<sub>3</sub> and D + ND<sub>3</sub><sup>a</sup>

species	moments of inertia, 10 <sup>-47</sup> kg m <sup>2</sup>	vib freq, cm <sup>-1</sup>
NH3	2.75, 2.75, 4.36	1079, 1651, 1651, 3294, 3413, 3413
NH₄⁺	3.20, 10.75, 11.86	645, 654, 1123, 1326, 1376, 1545, 3256, 3348, 2529 <i>i</i>
$ND_3$	5.32, 5.32, 8.71	820, 1199, 1199, 2354, 2513, 2513
ND₄‡	6.16, 20.15, 22.62	457, 465, 846, 953, 1001, 1131, 2353, 2465, 1821 <i>i</i>

<sup>a</sup>Calculations by C. F. Melius, ref 8.

TABLE II	I: Input	Data for	<b>Transition-State Theory</b>	<b>Calculations</b>	on
the Reaction	ons H +	NH <sub>3</sub> and	$D + ND_3$		

	5 5	
	Enthalpies of Formation	
Н	$\Delta H_{\rm f}^{\circ}{}_0 = 216 \text{ kJ mol}^{-1}$	ref 10
$NH_3$	$\Delta H_{\rm f}^{\circ}{}_0 = -39 \text{ kJ mol}^{-1}$	ref 10
NH <sub>2</sub>	$\Delta H_{\rm f}^{\circ}{}_0 = 192 \text{ kJ mol}^{-1}$	ref 11
	Vibrational Frequencies	
$H_2$	$\nu = 4401 \text{ cm}^{-1}$	ref 12
$D_2$	$\nu = 3116 \text{ cm}^{-1}$	ref 12
$\overline{NH}_2$	$\nu = 3173, 1497, 3220 \text{ cm}^{-1}$	ref 13
$ND_2$	$\nu = 2305, 1110, 2367 \text{ cm}^{-1}$	ref 13
En	ergy Barriers and Eckart Parame	ters
$H + NH_3$	$\Delta E_1 = 65 \text{ kJ mol}^{-1}, \alpha_1 = 13.$	6, $\alpha_2 = 10.3$
$D + ND_3$	$\Delta E_2 = 67 \text{ kJ mol}^{-1}, \alpha_1 = 19.$	4, $\alpha_2 = 14.5$

on the different masses involved to derive parameters for the D + ND<sub>3</sub> system, as shown in Tables II and III. We employ the conventional TST formalism<sup>14</sup>

<sup>(8)</sup> Melius, C. F., personal communication, Jan 1987.

<sup>(9)</sup> The recent BAC-MP4 calculations (ref 8) for the reactions  $H + NH_3$ and  $D + ND_3$  yielded different vibrational frequencies from those used in ref 1 and 2 for  $H + NH_3$  only. We therefore use these newer results to make slightly more refined estimates of rate coefficients for reaction 1 as well as reaction 2. The values obtained for  $k_1$  are very close to those derived in ref 1.

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$$k_i(T) = \Gamma^* l^{\ddagger}(k_{\rm B}T/h)(Q_i^{\ddagger}/Q_iQ_i') \exp(-\Delta E_i/RT)$$
(6)

Here *i* is to be read as 1 or 2 depending on whether the  $H + NH_3$ or  $D + ND_3$  reaction is considered.  $\Gamma^*$  is a tunneling transmission coefficient, which does not allow for recrossing of the saddle point of the potential energy surface.  $l^{t}$  is the reaction path degeneracy (3 here), and  $Q_i^{\dagger}$  and  $Q_i$ ,  $Q_i'$  represent partition functions, excluding rotational symmetry numbers, for the transition state and reactants.  $\Delta E_i$  represents the energy change including zero-point energy going from reactants to transition state for reaction i at 0 K.

C. F. Melius<sup>8</sup> has estimated properties of the activated complexes for reactions 1 and 2 using his ab initio BAC-MP4 method.<sup>15,16</sup> The geometry has been given already,<sup>17</sup> and moments of inertia and vibrational frequencies used to derive  $Q_i^{\dagger}$  are listed in Table II. BAC-MP4 yields  $\Delta E_1 \approx 56 \text{ kJ mol}^{-1,8}$  but because the uncertainty in this value may be estimated<sup>16</sup> as  $10-20 \text{ kJ mol}^{-1}$ , we treat  $\Delta E_1$  as a somewhat adjustable parameter.  $\Delta E_1$  is found to be 65 kJ mol<sup>-1</sup> by fitting to  $k_1$  at 1000 K. We choose this temperature because it is in the range where tunneling is only weakly dependent on  $\Delta E_1$  and where the previous measurements of  $k_1$  overlap.<sup>1-3</sup> Then,  $\Delta E_2 = 67$  kJ mol<sup>-1</sup> is derived from  $\Delta E_1$ by taking into account changes in zero-point energy for reactants (Table II) and products (Table III).

We estimate  $\Gamma^*$  in a way we found suitable for reaction 1,<sup>1</sup> i.e., by fitting an Eckart potential to the vibrationally adiabatic reaction coordinate at 0 K.<sup>18,19</sup> Limitations of deriving  $\Gamma^*$  from an Eckart barrier arise from uncertainty in the BAC-MP4 estimation of the imaginary frequency, as well as the approximation of simplifying the full multidimensional potential surface to a one-dimensional reaction coordinate through the saddle point. We find the Eckart parameters<sup>19</sup>  $\alpha_1$  and  $\alpha_2$  shown in Table III for each reaction from the forward and reverse barrier heights. These heights are calculated from  $\Delta E_i$ , together with the exothermicity of reaction 1

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(18) Eckart, C. Phys. Rev. 1930, 35, 1303.

(19) Johnston, H. S. Gas Phase Reaction Rate Theory; Ronald: New York, 1966; Chapter 2. There is a typographical error in its eq 2-22: the  $2\pi^2/16$  term should be  $4\pi^2/16$ .

and the zero-point energies as derived from the data of Tables II and III.

Equation 6 is evaluated over the range 500-2500 K: results may be fitted to within 10% by the expressions

$$k_1(T) =$$
  
1.04 × 10<sup>-21</sup>(T/K)<sup>3.275</sup> exp(-4290 K/T) cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>  
(7)

$$k_2(T) =$$
  
2.46 × 10<sup>-19</sup>(T/K)<sup>2.61</sup> exp(-6070 K/T) cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>  
(8)

Figure 1 shows that theory and experiment agree quite well for  $k_2(T)$  over the entire investigated range and for  $k_1(T)$  especially at the lower and upper regions of the experimental range.

We have also calculated rate coefficients on the basis that tunneling is negligible, which requires  $\Delta E_1 = 60 \text{ kJ mol}^{-1}$  for fitting to  $k_1(1000 \text{ K})$  and thus  $\Delta E_2 = 62 \text{ kJ mol}^{-1}$ . The results for  $k_2(T)$ are too close to eq 8 to be clearly distinguishable in Figure 1 and are therefore not shown. Such very close agreement for reaction 2 is not surprising, since an alternative way to take small degrees of tunneling into account is simply to set  $\Gamma^* \approx 1$  and reduce the  $\Delta E$  term of eq 6.<sup>20</sup> Therefore, by contrast to the TST results for  $k_1(T)$ , our estimated  $k_2(T)$  values are only marginally dependent on the tunneling model assumed.

We conclude that a single surface plus a conventional TST treatment coupled with a simple tunneling model can be used to calculate rate coefficients for the reactions  $H + NH_3$  and D +ND<sub>3</sub>, which are in reasonable agreement with experimental data. This is in accord with a judgment reached recently for a number of further processes where H or D is abstracted from  $H_2$  or  $D_2$ .<sup>21</sup> The idea that tunneling contributes significantly to the rates of H-transfer reactions even at elevated temperatures agrees with our interpretations of the reactions  $H + N_2O$  and  $O + H_2/D_2$ , which show strong non-Arrhenius behavior attributed to tunneling.16,22

Acknowledgment. This work was supported by the U.S. Army Research Office. Special thanks are due to Dr. C. F. Melius for allowing us to quote unpublished results and for helpful criticism and to W. F. Flaherty and T. P. Hanna for technical assistance.

Registry No. D, 16873-17-9; ND<sub>3</sub>, 13550-49-7; D<sub>2</sub>, 7782-39-0.

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