Shock Tube Determination of the Overall Rate of NH₂ + NO → Products in the Thermal De-NOx Temperature Window

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ABSTRACT: The rate coefficient of the reaction $NH_2 + NO \rightarrow products (R1)$ was determined in shock tube experiments using frequency-modulation absorption spectroscopy for detection of NH_2 . Because of the sensitivity of the diagnostic system, very low reactant concentrations could be employed in order to reduce the influence of secondary reactions on the NH_2 profiles. Benzylamine, $C_6H_5CH_2NH_2$, was used as a thermal source of the NH_2 radicals in the experiments. To determine the reaction rate, a perturbation strategy was employed that is based on changes in the NH_2 profiles when NO is added to the $C_6H_5CH_2NH_2/Ar$ mixtures. The measured NH_2 profiles were interpreted by detailed kinetic modeling to obtain the overall reaction rate of R1 in the temperature range 1262–1726 K. The lower temperature limit of the present study is in the middle of the Thermal De-NOx temperature window. The present rate measurements are consistent with both our previous determination of the rate at higher temperatures and lower temperature data. A rate expression obtained by combining our higher temperature data and lower temperature data is

$$k_1 = 6.83 \times 10^{15} \,\mathrm{T}^{-1.203} \,e^{106/\mathrm{T}(\mathrm{K})} \,\mathrm{cm}^3 \,\mathrm{mol}^{-1} \,\mathrm{s}^{-1}$$

for the temperature range 200–2500 K. The estimated uncertainty of the rate coefficient is $\pm 20\%$. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 33: 715–721, 2001

INTRODUCTION

The Thermal De-NOx and reburning processes are used to reduce nitrogen oxide emissions from stationary

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combustion systems. In these processes, the reaction of NH_2 with NO plays an important role, and this reaction has two major product channels [1,2]. One is a chain branching channel

$$NH_2 + NO \rightarrow NNH + OH$$
 (R1a)

and the other is a chain terminating channel

$$NH_2 + NO \rightarrow N_2 + H_2O$$
 (R1b)

We wish Simon Bauer the happiest 90th birthday, and we salute his long list of contributions to science.

Two important kinetic parameters in modeling the Thermal De-NOx process are the overall rate coefficient of the NH₂ + NO reaction, $k_1 = k_{1a} + k_{1b}$, and the branching ratio, $\alpha = k_{1a}/k_1$. As a result of many experimental and theoretical studies, a consensus exists for the branching ratio, α , in the temperature range 300-2000 K [3,4]. As for the overall rate coefficient, k_1 , the low temperature studies show consistent results, but two issues remain for temperatures above 1400 K. The first issue is uncertainty in the absolute value of k_1 at high temperatures, where there are significant discrepancies among the experimental studies. The second is the temperature dependence of this rate coefficient. Deppe et al. [5] and Roose et al. [6] reported a positive temperature dependence, while Miller and Klippenstein reported a negative temperature dependence in their theoretical study [7]. Recently, Song and coworkers measured k_1 with small uncertainty in the temperature range 1716-2507 K and observed no evidence of a positive temperature dependence for this reaction [8]. However, there still is a need for data at temperatures below 1400 K because the Thermal De-NOx process is very sensitive to this reaction rate coefficient and the branching ratio in the Thermal De-NOx temperature window (1100-1400 K). The objective of the present study is to measure k_1 values in the Thermal De-NOx window.

METHOD OF APPROACH

We have employed a frequency-modulation (FM) absorption technique [9–11] for the sensitive detection of NH₂ radicals in shock tube experiments. In our previous study, monomethylamine (CH₃NH₂) was used as a source of the NH₂ radical [8]. However, CH₃NH₂ is not suitable for low temperature experiments since the decomposition rate of CH₃NH₂ below 1700 K is too slow to produce sufficient NH₂ radicals for our experimental conditions. In the present study, we used benzylamine (C₆H₅CH₂NH₂) that decomposes rapidly at lower temperatures to produce NH₂ radical.

A perturbation method was applied to reduce the uncertainty resulting from the influence of secondary reactions. First, a set of pyrolysis experiments of $C_6H_5CH_2NH_2$ in Ar was performed behind reflected shock waves, and the NH₂ mole fraction was measured as a function of time. Initially, $C_6H_5CH_2NH_2$ rapidly decomposes to produce NH₂ and $C_6H_5CH_2$ via

$$C_6H_5CH_2NH_2 \rightarrow C_6H_5CH_2 + NH_2$$
 (R2)

After reaching a maximum value, the NH₂ slowly decays, reacting with itself and other products of the decomposition process. Next, NO was added to the

 $C_6H_5CH_2NH_2/Ar$ mixture and experiments were performed at nearly identical conditions as those for the $C_6H_5CH_2NH_2$ pyrolysis experiments. In this case, the, NH_2 profile is perturbed by the added NO, and the decay rate of NH_2 increases significantly because of the reaction of NH_2 with NO (see Fig. 1).

To determine k_1 values, the perturbed NH₂ profiles were interpreted using a detailed 63-reaction mechanism that was optimized by analyzing the $C_6H_5CH_2NH_2$ pyrolysis data (see Table I). This reaction mechanism comprises relevant reactions from Thermal De-NOx chemistry [4,16] and toluene, benzyl [12,13], and cyclopentadiene [14] pyrolysis mechanisms.

In the first step of the perturbation method, we performed NH₂-sensitivity analysis [17] and chose the key reactions whose rate coefficients were adjusted to optimize the base mechanism for benzylamine pyrolysis. A result of NH₂-sensitivity analysis for a C₆H₅CH₂NH₂/Ar experiment is shown in Fig. 2. At this experimental condition, the C6H5CH2NH2 decomposition (R2) is important for NH₂ production, and the NH₂ decay is sensitive to R8, R28, and R30. At lower temperatures, the reaction between C₆H₅CH₂NH₂ and NH₂ (R5) is important. As temperature increases, the NH2 becomes more sensitive to reactions between fragments of the benzyl radical, C₆H₅CH₂, and the NH₂ radical because C6H5CH2 starts to decompose at high temperature. We assumed that C₅H₅, C₄H₄, C₃H₃, and C₂H₂ were fragments of C₆H₅CH₂ and included



Figure 1 Example NH₂ mole fraction profiles: (a) 30 ppm C₆H₅CH₂NH₂/0%NO/Ar balance, T = 1488 K, P = 1.37 bar; (b) 30 ppm C₆H₅CH₂NH₂/900 ppm NO/Ar balance, T = 1491 K, P = 1.39 bar. Solid lines are best fits to the data using a detailed kinetic model (Table I). Broken lines are $\pm 10\%$ variation in k_1 .

	Reaction	Α	n	E_{a}	Ref.
R1a	$NH_2 + NO \rightarrow NNH + OH$	4.29E10	0.294	-3639	See text
R1b	$NH_2 + NO \rightarrow N_2 + H_2O$	2.61E19	-2.369	3624	See text
R2	$C_6H_5CH_2NH_2 \leftrightarrow C_6H_5CH_2 + NH_2$	5.49E14	0.00	275300	See text
R3	$C_6H_5CH_2NH_2 + H \rightarrow C_6H_5CHNH_2 + H_2$	5.00E13	0.00	33500	est.
R4	$C_6H_5CH_2NH_2 + NH \rightarrow C_6H_5CHNH_2 + NH_2$	1.00E13	0.00	20900	est.
R5	$C_6H_5CH_2NH_2 + NH_2 \rightarrow C_6H_5CHNH_2 + NH_3$	4.00E12	0.00	0	est.
R6	$C_6H_5CH_2 + NH_2 \rightarrow C_6H_5CH + NH_3$	1.00E12	0.00	12600	est.
R7	$C_6H_5CH_2 + NH \rightarrow C_6H_5CH + NH_2$	1.00E13	0.00	21000	est.
R8	$C_6H_5CH_2 + H \rightarrow C_6H_5CH_3$	2.00E14	0.00	0	[12]
R9	$2C_6H_5CH_2 \leftrightarrow C_6H_5CH_2CH_2C_6H_5$	5.00E12	0.00	1930	[12]
R10	$C_6H_5CH_2 \rightarrow C_5H_5 + C_2H_2$	2.51E16	0.00	407522	[13]
R11	$C_6H_5CH_2 \rightarrow C_4H_4 + C_3H_3$	1.26E16	0.00	405848	[13]
R12	$\mathrm{C_5H_5} + \mathrm{C_5H_5} \rightarrow \mathrm{C_{10}H_8} + 2\mathrm{H}$	2.00E13	0.00	16711	[14]
R13	$C_5H_5 \rightarrow C_5H_5-3$	3.90E11	1.00	322599	[14]
R14	$C_5H_5 \rightarrow C_5H_5$ -3b	2.90E11	1.00	321771	[14]
R15	$C_5H_5-3 \rightarrow C_2H_2 + C_3H_3$	1.40E11	1.00	123884	[14]
R16	$C_5H_5\text{-}3b \rightarrow C_2H_2 + C_3H_3$	3.00E11	1.00	140599	[14]
R17	$C_2H_2 + NH_2 \rightarrow HCN + CH_3$	3.70E12	0.00	47400	[15]
R18	$\rm C_4H_4 \rightarrow \rm C_4H_3 + \rm H$	2.00E11	0.00	251000	[12]
R19	$C_4H_4 \rightarrow 2C_2H_2$	1.00E13	0.00	334700	[12]
R20	$C_4H_4 \rightarrow C_4H_2 + H_2$	1.00E13	0.00	305400	[12]
R21	$\rm C_4H_3 \rightarrow \rm C_4H_2 + \rm H$	2.00E11	0.00	213400	12]
R22	$C_4H_3 + H \rightarrow C_4H_2 + H_2$	2.00E14	0.00	60700	[12]
R23	$C_4H_4 + H \rightarrow C_4H_3 + H_2$	3.02E14	0.00	60700	[12]
R24	$C_5H_5 + NH_2 \rightarrow C_5H_6 + NH$	5.00E12	0.00	0	est.
R25	$\rm C_3H_3 + \rm NH_2 \rightarrow \rm C_3H_2 + \rm NH_3$	1.50E13	0.00	0	est.
R26	$\rm C_3H_3 + NH_2 \rightarrow C_3H_4 + NH$	1.50E13	0.00	0	est.
R27	$\rm C_4H_4 + \rm NH_2 \rightarrow \rm C_4H_5 + \rm NH$	5.00E12	0.00	0	est.
R28	$\rm NH_2 + \rm H \leftrightarrow \rm NH + \rm H_2$	5.00E13	0.00	15272	See text
R29	$NH_2 + NH \leftrightarrow N_2H_2 + H$	5.00E13	0.00	0	[16]
R30	$NH_2 + NH_2 \leftrightarrow NH_3 + NH$	5.48E14	0.00	79200	See text
R31	$\rm NH_2 + \rm NH_2 \leftrightarrow \rm N_2H_2 + \rm H_2$	2.00E11	0.00	0	See text
R32	$NH_2 + NH_2 (+M) \leftrightarrow N_2H_4 (+M)$	1.50E13	0.00	0	[16]
R33	$NH_2 + OH \leftrightarrow NH + H_2O$	4.00E06	2.00	4184	[16]
R34	$NH_3 + M \leftrightarrow NH_2 + H + M$	2.20E16	0.00	391078	[16]
R35	$NH_3 + H \leftrightarrow NH_2 + H_2$	6.40E05	2.39	42555	[16]
R36	$NH_3 + O \leftrightarrow NH_2 + OH$	9.40E06	1.94	27029	[16]
R37	$NH_3 + OH \leftrightarrow NH_2 + H_2O$	2.00E06	2.04	2368	[16]
R38	$NH_3 + HO_2 \leftrightarrow NH_2 + H_2O_2$	3.00E11	0.00	92048	[16]
R39	$N_2H_4 + H \leftrightarrow N_2H_3 + H_2$	1.30E13	0.00	10460	[16]
R40	$N_2H_4 + O \leftrightarrow N_2H_2 + H_2O$	8.50E13	0.00	5021	[16]
R41	$N_2H_4 + OH \leftrightarrow N_2H_3 + H_2O$	4.00E13	0.00	0	[16]
R42	$N_2H_4 + NH_2 \leftrightarrow N_2H_3 + NH_3$	3.90E12	0.00	6276	[16]
R43	$N_2H_3 + M \leftrightarrow N_2H_2 + H + M$	3.50E16	0.00	192464	[16]
R44	$N_2H_3 + H \leftrightarrow NH_2 + NH_2$	1.60E12	0.00	0	[16]
R45	$N_2H_3 + O \leftrightarrow N_2H_2 + OH$	5.00E12	0.00	20920	[16]
R46	$N_2H_3 + O \leftrightarrow NH_2 + HNO$	1.00E13	0.00	0	[16]
R47	$N_2H_3 + OH \leftrightarrow N_2H_2 + H_2O$	1.00E13	0.00	4184	[16]
K48	$N_2H_3 + OH \leftrightarrow NH_3 + HNO$	1.00E12	0.00	62760	[16]
K49	$N_2H_3 + NH \leftrightarrow N_2H_2 + NH_2$	2.00E13	0.00	0	[16]
K50	$N_2H_2 + M \leftrightarrow NNH + H + M$	5.00E16	0.00	209200	[16]
K31 D52	$N_2H_2 + H \leftrightarrow NNH + H_2$	5.00E13	0.00	4184	[16]
K52 D52	$N_2H_2 + O \leftrightarrow NH_2 + NO$	1.00E13	0.00	4184	[16]
кээ	$N_2 n_2 + O \leftrightarrow NNH + OH$	2.00E13	0.00	4184	[16]

 Table I
 Reaction Mechanism Used for Data Analysis

Continued

Table I	Continued
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	Reaction	Α	п	Ea	Ref.
R54	$N_2H_2 + OH \leftrightarrow NNH + H_2O$	1.00E13	0.00	4184	[16]
R55	$N_2H_2 + NO \leftrightarrow N_2O + NH_2$	3.00E12	0.00	0	[16]
R56	$N_2H_2 + NH \leftrightarrow NNH + NH_2$	1.00E13	0.00	4184	[16]
R57	$N_2H_2 + NH_2 \leftrightarrow NNH + NH_3$	1.00E13	0.00	4184	[16]
R58	$NNH \leftrightarrow N_2 + H$	6.70E07	0.00	0	[4]
R59	$NNH + H \leftrightarrow N_2 + H_2$	1.00E14	0.00	0	[16]
R60	$NNH + OH \leftrightarrow N_2 + H_2O$	5.00E13	0.00	0	[16]
R61	$NNH + NH \leftrightarrow N_2 + NH_2$	5.00E13	0.00	0	[16]
R62	$NNH + NH_2 \leftrightarrow N_2 + NH_3$	5.00E13	0.00	0	[16]

The rate constant are given by $k = AT^n \exp(-E_a/RT)$ in cm³, mol, s, J units.

reactions between these radicals and NH_2 in the reaction mechanism.

$$\begin{array}{c} C_6H_5CH_2NH_2 \rightarrow NH_2 \rightarrow C_6H_5CH_2NH + NH_3 \\ (R5) \end{array}$$

$$C_6H_5CH_2 + H \rightarrow C_6H_5CH_3 \tag{R8}$$

$$NH_2 + H \rightarrow NH + H_2$$
 (R28)

$$NH_2 + NH_2 \rightarrow NH_3 + NH$$
 (R30)

The rate coefficient of the $C_6H_5CH_2NH_2$ decomposition reaction (R2) was determined using the initial slope of the measured NH₂ trace. According to the RRKM calculations, R2 is in the fall-off region for the experimental conditions of the present study, so the rate expression of R2 in Table I is valid only for temperature range 1250–1750 K and pressure range 1.1–1.4 bar. The results of our study of $C_6H_5CH_2NH_2$



Figure 2 Results from NH₂ sensitivity analyses for the conditions of Fig. 1a: 30 ppm C₆H₅CH₂NH₂/0%NO/Ar balance, T = 1488 K, P = 1.37 bar.

decomposition reaction will be reported separately. As for rate coefficients of R28 and R31, the literature values [16] were slightly modified for the purpose of optimization of the reaction mechanism. The initial value of the reaction rate of R30 was taken from our previous study [8] and adjusted slightly during the optimization procedure for $C_6H_5CH_2NH_2$ pyrolysis experiments. Most of the other reaction rates were taken from literature. However, some of reaction rates that were not available in the literature were estimated.

As mentioned previously, our goal was to determine k_1 values, and the reaction mechanism was optimized to predict NH₂ profiles during C₆H₅CH₂NH₂ pyrolysis under specific experimental conditions. Therefore, the reaction mechanism reported in Table I should be used only for the range of conditions of the present study.

Figure 3 shows a NH_2 sensitivity plot for a $C_6H_5CH_2NH_2/NO/Ar$ experiment. The most important



Figure 3 Results from NH₂ sensitivity analyses for the conditions of Fig. 1b: 30 ppm $C_6H_5CH_2NH_2/900$ ppm NO/Ar balance, T = 1491 K, P = 1.39 bar.

reaction is the NH₂ + NO reaction. While the NH₂ trace is sensitive to the C₆H₅CH₂NH₂ decomposition reaction (R2) during the very early stage of reaction, this reaction has a very small effect on the k_1 determination because R1 and R2 are decoupled in terms of time. In addition, the sensitivity to the branching ratio is small compared with R1. Therefore, any uncertainty in the branching ratio does not have a significant effect on the k_1 determination.

EXPERIMENTAL

Experiments were performed behind reflected shock waves in a stainless steel shock tube (15.4 cm inside diameter, 10.5 m long driven section, and 3.7 m long driver section). To reduce impurities and residue, the shock tube was evacuated to an ultimate pressure of 2.5×10^{-7} torr using a turbomolecular pump before each experiment, and the combined leak and outgassing rate was typically 4×10^{-6} torr min⁻¹. The diagnostic laser beam passes through the optical windows, which are located at 2 cm apart from the endwall. Temperature and pressure behind the reflected shock wave were calculated from the initial temperature and pressure, and the shock speed measured over four intervals using five piezoelectric pressure gauges. The estimated uncertainty in reflected shock temperature was less than ± 20 K at 1400 K over the time intervals of interest.

Liquid C₆H₅CH₂NH₂ (>99.5%, Aldrich) was evaporated in a temperature-controlled bubble saturator, from which a mixture of Ar (>99.9999%, Praxair) and $C_6H_5CH_2NH_2$ vapor was continuously supplied to the shock tube. The flow scheme used in the present study reduces the uncertainty in the initial concentration of $C_6H_5CH_2NH_2$ due to wall adsorption. To measure the actual concentration of the C₆H₅CH₂NH₂ entering the shock tube, absorption of C₆H₅CH₂NH₂ was measured between the bubble saturator and the shock tube using a 3.39 µm He–Ne laser. A commercially available NO/Ar mixture (1.98% of NO, Praxair) was used in the perturbation experiments. The NO₂ and N₂O impurities in the NO/Ar mixture were measured using an FTIR. The mole fractions of NO2 and N2O were 42 and 51 ppm, respectively. The influence of the NO_2 and N_2O impurities on the k_1 determination is negligible for the conditions of the present study.

To measure the NH₂ concentration, we used a FM absorption technique. A detailed description of the FM absorption setup used in the present study was given by Vostsmeier et al. [18]. With FM absorption, at least a factor of 10 reduction in the NH₂ detection limit can be achieved in comparison with direct laser absorption. Consequently, the initial concentration of

 $C_6H_5CH_2NH_2$ can be decreased to reduce the influence of secondary reactions.

RESULTS AND DISCUSSION

Experiments were conducted in the temperature range 1262-1726 K. The pressure was between 1.14 and 1.45 bar. In total, 44 NH_2 traces from $C_6H_5CH_2NH_2$ and NO experiments were analyzed. The initial concentration of benzylamine was varied from 20 to 40 ppm, and the ratio of NO to $C_6H_5CH_2NH_2$ from 11 to 60. As shown in Fig. 4, no systematic effect on the k_1 determination was observed when different initial concentrations of NO in the mixture or different ratios of NO to C₆H₅CH₂NH₂ were used. Consequently, the results of our experiments are independent of the initial concentration of NO and the ratio of NO to C₆H₅CH₂NH₂ in the initial gas mixture. In addition, the results of C₆H₅CH₂NH₂ experiments are consistent with those of our previous study using CH₃NH₂ [8]. The vertical error bars in Fig. 4 indicate the combined uncertainties, which include fitting errors, influence of uncertainties of other reaction rate parameters, and uncertainties in the NH₂ absorption coefficient at the wavelength of interest. The combined uncertainties depend on temperature and vary from $\pm 12\%$ (at 1432 K) to $\pm 17\%$ (at 1726 K). The major source of uncertainty at low



Figure 4 Comparison of the results of C₆H₅CH₂NH₂ and CH₃NH₂ experiments. Data from C₆H₅CH₂NH₂ experiments: ■ 300 ppm NO; ● 500 ppm NO; ▲ 600 ppm NO; ▼ 800 ppm NO; ● 900 ppm NO; + 0.12% NO; □ data from CH₃NH₂ experiments [8]; --- Eq. (1). The vertical bars represent the combined fitting errors and uncertainties associated with secondary reactions and absorption coefficient.

temperature (below 1350 K) is uncertainties in the reaction rates of the secondary reactions including R2. At mid and high temperatures (above 1350 K), the contribution of the fitting error and the uncertainties in chemistry to the total uncertainty is comparable. The k_1 values are tabulated in Table II together with the experimental conditions.

Table IISummary of k_1 with Experimental Conditions

T (K)	P (bar)	$x_{\rm BA}$ (ppm)	$x_{\rm NO}$ (ppm)	$\log_{10} k_1$ (cm ³ mol ⁻¹ s ⁻¹)
1262	1.24	40	520	12.15
1202	1.24	40	530	12.15
1200	1.28	40	530	12.14
1207	1.27	40	530	12.15
12/0	1.20	41	530	12.13
1201	1.20	40	530	12.14
1203	1.20	42	330	12.12
1290	1.29	20	520	12.13
1299	1.23	40	530	12.13
1304	1.24	35	530	12.12
1305	1.34	20	880	12.12
1320	1.27	22	880	12.11
1320	1.24	20	900	12.11
1349	1.41	28	880	12.10
1351	1.32	41	530	12.10
1352	1.14	29	320	12.09
1355	1.29	31	900	12.09
1358	1.28	31	900	12.08
1359	1.32	30	900	12.08
1367	1.32	29	900	12.07
1390	1.45	27	890	12.09
1422	1.26	27	320	12.07
1427	1.42	27	900	12.06
1428	1.44	27	610	12.04
1432	1.41	29	610	12.06
1447	1.33	26	880	12.04
1473	1.30	30	320	12.04
1488	1.39	30	880	12.03
1491	1.40	30	880	12.03
1507	1.41	24	880	12.02
1530	1.43	24	880	12.02
1548	1.24	20	810	12.03
1550	1.28	19	810	12.01
1565	1.35	26	880	11.99
1565	1.30	21	810	12.01
1580	1.24	19	810	12.01
1590	1.28	19	810	12.03
1607	1.33	26	880	11.99
1616	1.28	20	1190	12.00
1661	1.32	20	1190	11.99
1669	1.30	19	810	11.97
1681	1.34	21	1200	11.99
1682	1.27	20	810	12.00
1703	1.24	21	810	11.97
1726	1.29	20	810	11.97

Our C₆H₅CH₂NH₂ and CH₃NH₂ data are consistent with the lower temperature data as shown in Fig. 5. Combination of our high temperature data with lower temperature data from the most recent flow reactor experiments of Wolf et al. [25] results in the following expression for k_1 in the temperature range 200– 2500 K.

$$k_1 = 6.83 \times 10^{15} T^{-1.203} e^{106/T \text{ (K)}} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
 (1)

1

The uncertainty in the given rate coefficient is estimated to be $\pm 20\%$. Compared with the theoretical results of Miller and Klippenstein [7], the current k_1 rate expression is yields values about 25% lower than their k_1 values in the Thermal De-NOx temperature window.

In our previous study of the branching ratio, we noted that the branching ratio determination depends slightly on the overall rate of the NH₂ + NO reaction [3]. With the new values of k_1 given by Eq. (1), the earlier branching ratio data were reevaluated. As seen in Fig. 6, the effect of k_1 on the branching ratio determination is very small, and the updated branching ratio shows even better agreement with branching ratio from Miller and Klippenstein's theoretical work [7]. For modeling purposes, we suggest the following rate expressions for R1a and R1b, which were calculated using their branching ratio results data [7] and the



Figure 5 Summary of k_1 : Data from C₆H₅CH₂NH₂ experiments; \Box data from CH₃NH₂ experiments [8]; O [19]; \triangle [20]; \bigtriangledown [21]; \diamond [22]; + [23]; × [24]; ***** [25]; — [7]; - - Eq. (1). The vertical bars represent the combined fitting errors and uncertainties associated with secondary reactions and absorption coefficient.



Figure 6 Reevaluation of the branching ratio: \blacksquare updated branching ratio using Eq. (1); \square [3]; - [7].

overall rate coefficient given by Eq. (1).

$$k_{1a} = 4.29 \times 10^{10} T^{0.294} e^{438/T \text{ (K)}} \text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (2)$$

$$k_{1b} = 2.61 \times 10^{19} T^{-2.369} e^{-436/T \text{ (K)}} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (3)$$

These rate expressions are valid for temperature range 400–1900 K. In this temperature range, the sum of k_{1a} and k_{1b} slightly deviates from k_1 in Eq. (1) by less than 5%.

CONCLUSION

Frequency-modulation absorption spectroscopy and a perturbation method were employed in shock tube experiments to obtain an accurate determination of the overall rate of the NH₂ + NO reaction in the temperature range 1262–1726 K. Use of C₆H₅CH₂NH₂ as an NH₂ source allowed extension of the k_1 determination to the Thermal De-NOx temperature window. A new expression for k_1 is recommended which provides a consistent fit to k_1 data over the temperature range 200–2500 K and updated rate expressions for two product channels of the NH₂ + NO reaction were obtained for the temperature range 400–1900 K.

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