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Branching Fraction of the $NH_2 + NO$ Reaction between 1210 and 1370 K

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The branching fraction for the $NH_2 + NO$ reaction has been determined in the temperature range 1210−1370 K from flow reactor experiments on the $NH_3/NO/O_2$ and $CO/NH_3/NO/O_2$ systems. The branching fraction is defined as $\alpha = k_1/(k_1 + k_2)$, where $NH_2 + NO \rightarrow NNH + OH$ (1) and $NH_2 + NO \rightarrow N_2 + H_2O$ (2). The experiments were performed at very low oxygen concentrations to minimize the impact of secondary reactions. The results show that α increases gradually from a value of 0.35 ± 0.04 at 1211 K to 0.45 ± 0.02 at 1369 K. The data blend smoothly with the most recent direct measurements and confirm the significant rise in branching fraction suggested by previous high-temperature determinations in static reactors and flames.

Introduction

Over the years significant efforts have been undertaken to develop a detailed reaction mechanism for the selective noncatalytic reduction of nitric oxide by ammonia.[1−7] This process, which was discovered by Lyon[8] in 1972 and coined thermal De−NO_x, is widely used as a practical NO_x control technique, but details of the reaction mechanism remain controversial.

The key reaction in thermal De−NO_x is the reaction between NH_2 and NO. This reaction has two major product channels, a radical-producing channel that presumably is[1,5,7]

$$NH_2 + NO \rightleftharpoons NNH + OH \qquad (1)$$

and a chain-terminating channel

$$NH_2 + NO \rightleftharpoons N_2 + H_2O \qquad (2)$$

A fairly large body of experimental data on the $NH_2 + NO$ reaction has been reported in literature. The overall rate coefficient is well established over a wide temperature range,[7] but the branching fraction, defined as $\alpha = k_1/(k_1 + k_2)$, remains uncertain. At room temperature a number of studies[9−14] support a value for α of approximately 0.11, and direct measurements[11−13,15] are in good agreement up to roughly 800 K. Data reported at higher temperatures show significant scatter, however, with values ranging roughly from 0.2 to 0.5 at 1200 K.[2,13,16]

The work on the $NH_2 + NO$ reaction can roughly be divided into two groups, depending on the way the NH_2 radicals are generated. A number of studies have used "clean" sources of NH_2 such as flash-photolysis,[11−13,17−24] discharge[9,10,25−28] or radiolysis[14,29,30] to generate the NH_2 radicals. These experiments, which are all performed in static or low-flow systems, are generally considered direct or "reaction-specific". A different approach is to generate the NH_2 radicals thermally. In this way the chemistry involved becomes more complex due to secondary reactions, and the experimental data require interpretation in terms of a complex chemical kinetic model. For this reason these experiments are often characterized as indirect or "non-reaction-specific" and the information obtained is generally regarded as more uncertain. For the $NH_2 + NO$ reaction such work includes batch reactor experiments,[16] flow reactor experiments,[2] and flame experiments.[31,32] However, at high temperatures the distinction between "direct" and "indirect" experiments becomes less clear, because secondary reactions become difficult to avoid. Indeed, it was suggested recently[24] that it was the occurrence of secondary reactions not accounted for that prompted Stephens et al.[13] to postulate the existence of a third product channel at high temperatures in their flash pyrolysis study of the $NH_2 + NO$ reaction.

Until very recently the data for the branching fraction of the $NH_2 + NO$ reaction appeared to fall into two groups, with the direct measurements[11−13] supporting comparatively low values of α, apparently in contradiction to indirect determinations[2,5−7,31,32] and theoretical studies,[33,34] which consistently favor a significant rise in branching fraction at higher temperatures. Recent direct measurements[15] as well as batch reactor results[16] to some extent bridge the gap between the "direct" and "indirect" data, but significant discrepancies remain in the 1000−1400 K range, i.e., in the temperature range for the thermal De−NO_x process.

The objective of the present work is to determine the branching fraction of the $NH_2 + NO$ reaction in the 1200−1400 K range from flow reactor experiments on the $NH_3/NO/O_2$ and $CO/NH_3/NO/O_2$ systems. At very low oxygen concentrations the NNH formed in reaction 2 always dissociates, and the temperature for onset of reduction of NO by NH_3 depends almost solely on the branching fraction of the $NH_2 + NO$ reaction.[7,34] The experimental data used in the analysis are obtained partially from new experiments reported here and partially from earlier studies in our laboratory.[35,36]

Experimental Section

Two different experimental flow reactor configurations were used in the present work, one setup used previously to study atmospheric pressure (AP) chemistry[35,37−39] and one that allows for high-pressure (HP) experiments.[36] In both configurations a quartz flow reactor designed to minimize dispersion is placed in a three-zone electrically heated oven, providing a uniform temperature profile within ±7 K over the reactor. The reactor temperature is measured by a thermocouple placed in a quartz tube with no access for the reactant gases. To achieve a well-defined reactor volume, the main flow, containing oxygen and nitrogen, and the injector flow(s) with the remaining reactants are heated separately and mixed in a cross flow at the reactor

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inlet. In the AP configuration water is added to the main flow by saturating nitrogen in a thermostatically controlled water bath, while in the HP setup the water is delivered to the injector stream by an HPLC pump in combination with an evaporation system. All tubes containing water vapor are heated above the dew point.

The reactor tubes used in the two configurations both have a volume of about 10 mL. After reaction the products are quenched by cold gas at the outlet of the reactor tube. The product gas is then led to a water condenser and finally to the gas analyzers. The two different reactor systems have been shown to provide reproducible and internally consistent results. More details about the flow reactor configurations and the experimental procedures can be found elsewhere.[36,38,39]

The concentrations of NO, CO, CO_2, and O_2 are measured continuously by spectrophotometric and paramagnetic analyzers, respectively, with an accuracy of ±3% but not less than ±10 ppmv.

High-temperature flow reactor experiments are usually not well suited for deriving specific information on elementary reactions in complex reaction systems. However, if the experiments are designed and conducted carefully, fairly accurate rate data can be obtained. Previous flow reactor work on elementary reactions using the AP setup has focused on N_2O dissociation,[40,41] the $N_2O + OH$ reaction,[41] and the $NH_2 + NO_2$ reaction.[42] The uncertainty associated with the flow reactor technique is discussed in detail elsewhere.[40,43] The major concerns are the uncertainty in the reactor temperature and mixing effects; surface effects in the quartz reactors are believed to be insignificant.[6,40,43]

Method of Analysis

At very low oxygen levels, the low-temperature boundary for removal of NO in thermal De−NO_x experiments is determined completely by the branching fraction α of the $NH_2 + NO$ reaction.[7] In the present work, flow reactor results on $NH_3/NO/O_2$ and $CO/NH_3/NO/O_2$ systems under carefully selected reaction conditions are used to extract values of α in the temperature range 1210−1370 K.

Our interpretation of the flow reactor data is based on plug-flow calculations performed with Senkin,[44] which runs in conjunction with the Chemkin library.[45] The plug-flow assumption has been shown to be valid for thermal DeNO_x experiments in the present flow reactor system.[6]

The reaction mechanism used in the present work is adopted without modifications from the work of Miller and Glarborg[7] on the thermal De−NO_x chemistry. To this reaction mechanism, which with a few important exceptions[7] is also identical with the scheme used in a recent analysis of the $NH_2 + NO_2$ reaction,[42] was added a small subset of CO oxidation reactions.[46] Thermodynamic data are taken from the Sandia Thermodynamic Database.[47] Miller and Glarborg[7] discuss in detail the key features of the mechanism, which has been validated over a significant range of temperature, oxygen concentration, and pressure.[7,36]

Results and Discussion

The experimental data used in the present work are shown in Figure 1 and the experimental conditions are summarized in Table 1. Eighteen data sets were considered: sets 1−4 and 12−18 are from the present work; sets 5−10 and set 11 were taken from Kasuya et al.[35] and from Kjærgaard,[36] respectively. The data comprise 11 sets on the $NH_3/NO/O_2$ system and 7 sets on the $CO/NH_3/NO/O_2$ system, all obtained at low O_2 concentrations (400−2000 ppm).

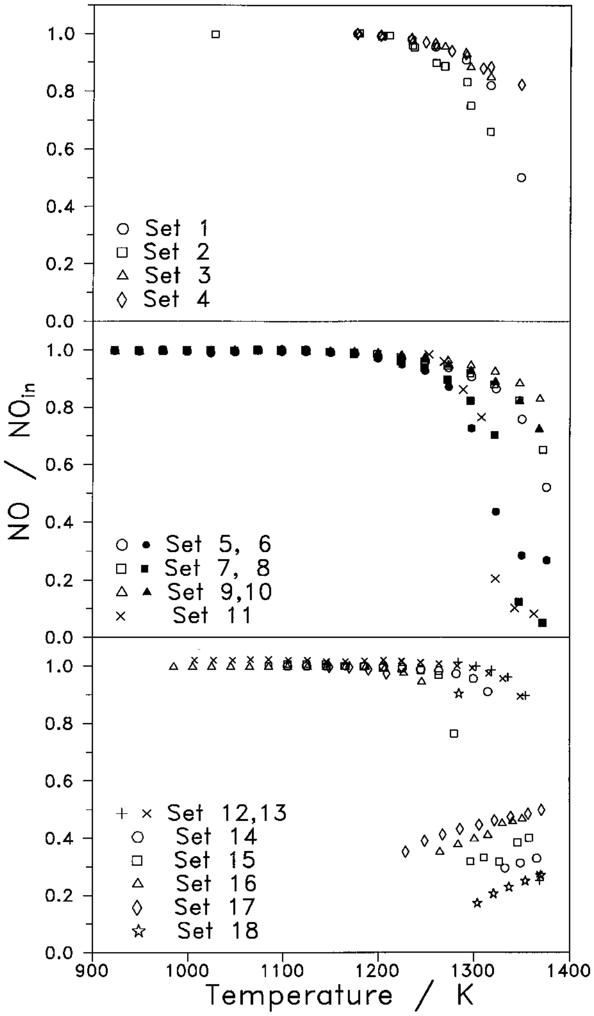

Figure 1. Flow reactor results for the concentration of NO as function of temperature in the $NH_3/NO/O_2$ and $CO/NH_3/NO/O_2$ systems. Reaction conditions as well as sources of data are listed in Table 1.

TABLE 1: Experimental Conditions[a]

set	NH_3 (ppm)	NO (ppm)	CO (ppm)	O_2 (ppm)	H_2O (vol %)	τ (s)	P (atm)	source
1	963	950		956	1.9	93[K]/T	1.25	pw
2	950	435		971	1.9	92[K]/T	1.25	pw
3	929	456		476	1.9	92[K]/T	1.25	pw
4	943	440		255	1.9	92[K]/T	1.25	pw
5	400	212		1000	5.0	88[K]/T	1.05	[33]
6	400	203		2000	5.0	88[K]/T	1.05	[33]
7	980	494		1000	5.0	88[K]/T	1.05	[33]
8	960	486		2000	5.0	88[K]/T	1.05	[33]
9	2800	1470		1000	5.0	88[K]/T	1.05	[33]
10	2800	1470		2000	5.0	88[K]/T	1.05	[33]
11	1001	491		1007	1.0	151[K]/T	1.25	[34]
12	403	406	699	399	1.9	125[K]/T	1.15	pw
13	403	406	699	399	2.0	125[K]/T	1.10	pw
14	404	413	699	603	2.0	121[K]/T	1.10	pw
15	396	404	1389	604	2.0	121[K]/T	1.10	pw
16	395	420	1388	800	2.0	121[K]/T	1.10	pw
17	395	403	1388	999	2.0	119[K]/T	1.10	pw
18	783	391	1346	968	2.0	115[K]/T	1.10	pw

[a] "pw" denotes present work. The experiments were conducted at constant mass flow rate. Thereby the residence time depends on the temperature, as listed.

For the present study it is convenient to characterize each experimental data set in terms of an "initiation temperature", i.e., the temperature at which NO first begins to disappear. We define the initiation temperature as the lowest temperature at which 10−20% of the NO is removed. The precise value used depends on the experimental conditions. Most of the experiments have a well-defined low-temperature boundary for reaction. For these experiments, either 10% NO removed (by linear interpolation between data points) or an actual data point (in the range 10−20% NO conversion) was used to define the initiation temperature. However, for a few of the data sets, in particular set 2, we consider the onset of reaction to be less well-defined due to scatter in the experimental data. For this experiment a higher fractional conversion of NO was chosen for the initiation temperature in order to minimize this uncertainty.

The predicted initiation temperature is so sensitive to the critical parameters in the model that this temperature can be used in a systematic manner to determine key kinetic parameters in the mechanism.[7] The low-temperature boundary for reaction is determined by the mix of chain-branching and chain-terminating reactions in the mechanism, primarily the competition between the two NH_2 + NO product channels:

$$NH_2 + NO \rightleftharpoons NNH + OH \qquad (1)$$

$$NH_2 + NO \rightleftharpoons N_2 + H_2O \qquad (2)$$

and the competition between spontaneous dissociation of NNH and the fast reaction with O_2:

$$NNH \rightleftharpoons N_2 + H \qquad (R90)$$

$$NNH + O_2\ N_2 + HO_2 \qquad (R126)$$

Here the reaction numbering refers to the listing of the mechanism in refs 36 and 42. The competition between NNH dissociation (R90) and reaction with O_2 (R126) is largely determined by the lifetime of NNH, which remains uncertain.[7] However, as emphasized by Miller and Glarborg,[7] at very low O_2 concentrations such as those employed in the present study, virtually all the NNH dissociates provided the experimental upper limit of 0.5 μ s[48] for the lifetime of NNH is accepted. Consequently, the initiation temperatures for the conditions of the present experiments are determined almost completely by the branching fraction of the NH_2 + NO reaction, and we can use these initiation temperatures to determine α.

For each set of experiments the initiation temperature and the corresponding NO mole fraction are identified. This particular datapoint is then matched with the model, keeping the total rate constant $k_T = k_1 + k_2$ for the NH_2 + NO reaction fixed and varying the branching fraction α. Two data sets, 3 and 4, were excluded from the analysis, because the initiation temperature could not be defined reliably.

The reaction conditions chosen and the corresponding values of the branching fraction extracted are shown in Table 2. The values of α as a function of temperature are also shown in Figure 2. The data cover temperatures in the range 1210−1370 K. The results show that α increases gradually from a value of 0.35 ± 0.04 at 1211 K to 0.45 ± 0.02 at 1369 K. Even though the experimental data are obtained in different studies and both the chemical composition and the flow reactor configuration vary, the scatter in the results is fairly small and clearly within the estimated uncertainty.

TABLE 2: Summary of Selected Experimental Conditions and Modeled Values for α for the $NH_3/NO/O_2$ and $CO/NH_3/NO/O_2$ Systems[a]

set	T(K)	χ(NO) (%)	$k_1/10^{11}$ (cm^3/mols)	α	α* ($\tau_{NNH} = 10^{-11}$ s)
1	1316	18	6.99	0.426 ± 0.028	0.413
2	1317	34	6.96	0.425 ± 0.020	0.416
3			data not considered		
4			data not considered		
5	1323	14	7.45	0.457 ± 0.028	0.455
6	1274	13	7.30	0.427 ± 0.033	0.410
7	1347	18	7.12	0.447 ± 0.020	0.449
8	1296	18	7.09	0.424 ± 0.028	0.412
9	1369	17	6.98	0.447 ± 0.020	0.456
10	1348	17	6.70	0.421 ± 0.020	0.425
11	1308	24	6.59	0.399 ± 0.021	0.388
12	1354	10	6.79	0.429 ± 0.023	0.430
13	1349	10	6.86	0.431 ± 0.022	0.433
14	1318	10	6.70	0.409 ± 0.025	0.406
15	1269	10	6.66	0.388 ± 0.032	0.382
16	1249	10	6.42	0.367 ± 0.039	0.358
17	1211	10	6.45	0.354 ± 0.039	0.341
18	1283	10	6.56	0.387 ± 0.028	0.379

[a] χ(NO) denotes the fractional conversion of NO at the condition chosen (the initiation temperature). α* is the estimated branching fraction assuming instantaneous dissociation of NNH.

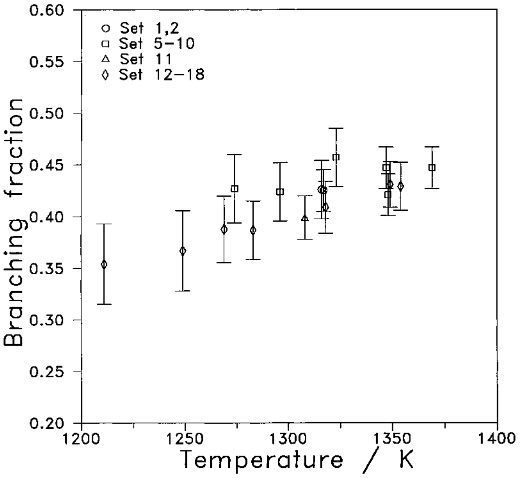

Figure 2. Branching fraction α for NH_2 + NO determined from flow reactor data in the temperature range 1210−1370 K.

The error analysis conducted includes three components: (1) an experimental uncertainty including uncertainty in inlet concentrations, outlet concentrations, and reactor temperature, (2) a first-order error analysis on the kinetic model (excluding NNH consumption reactions), and (3) the uncertainty associated with the uncertainty in the NNH lifetime. To evaluate the latter uncertainty, the flow reactor data were interpreted both in terms of our basis mechanism with a comparatively long lifetime for NNH (10^{-7} s, close to the experimental upper limit) and in terms of a mechanism with spontaneous dissociation of NNH, corresponding to a very fast rate for (R90). The resulting values of α are compared in Table 2. The good agreement between the two sets of α values confirms that the assumptions regarding the fate of NNH have little significance for the present study.

The most important component in the error analysis is the uncertainty associated with other important reactions in the kinetic model. A first-order sensitivity analysis for NO corresponding to the conditions of selected data sets is shown in Table 3. The sensitivity coefficients are generally displayed as

$$\beta_i = \frac{A_i}{X_{NO}} \frac{\partial X_{NO}}{\partial A_i}$$

where β_i is the sensitivity coefficient for change in the mole fraction of NO due to a small change in the temperature-independent factor of the ith reaction rate coefficient, A_i. However, for the NH_2 + NO reaction it is for present purposes more instructive to look at the sensitivity of NO to the total

TABLE 3: Normalized First-Order Sensitivity Coefficients for NO at the Initiation Temperature for Chosen Data Sets. Reaction Numbering Refers to the Listing of the Mechanism in Refs 36 and 42

	linear sensitivity coefficients for NO								
reaction	set 1 1316 K	set 5 1323 K	set 7 1347 K	set 8 1296 K	set 9 1369 K	set 11 1308 K	set 12 1354 K	set 15 1269 K	set 17 1211 K
$NH_2 + NO$ (branching fraction)	−12.11	−6.57	−16.96	−14.77	−13.32	−29.80	−2.64	−8.27	−6.12
$NH_2 + NO$ (total rate)	0.02	−0.23	−0.11	−0.01	0.01	0.23	0.04	0.34	0.29
2. $NH_3 + H \rightleftharpoons NH_2 + H_2$	0.56	0.03	0.15	0.20	0.20	1.40	0.05	0.27	0.25
4. $NH_3 + OH \rightleftharpoons NH_2 + H_2O$	0.00	−0.04	−0.03	−0.03	0.00	0.02	0.06	0.50	0.61
12. $NH_2 + O_2 \rightleftharpoons H_2NO + O$	−0.06	−0.09	−0.12	−0.14	−0.04	−0.16	−0.01	−0.02	−0.01
21. $NH_2 + NO_2 \rightleftharpoons H_2NO + NO$	−0.09	−0.02	−0.06	−0.09	−0.03	−0.22	0.00	−0.01	−0.01
36. $NO + O + M \rightleftharpoons NO_2 + M$	−0.06	−0.06	−0.19	−0.11	−0.16	−0.17	−0.03	0.02	0.07
39. $NO_2 + H \rightleftharpoons NO + OH$	0.21	0.01	0.06	0.08	0.11	0.42	0.01	0.03	0.05
90. $NNH \rightleftharpoons N_2 + H$	−0.34	−0.02	0.08	−0.26	0.20	−0.56	0.02	−0.09	−0.17
126. $NNH + O_2 \rightleftharpoons N_2 + HO_2$	0.34	0.02	−0.09	0.28	−0.24	0.59	−0.02	0.09	0.17
103. $H + O_2 \rightleftharpoons O + OH$	−2.32	−0.58	−1.30	−1.56	−0.81	−3.78	−0.35	−1.65	−1.49
105. $OH + H_2 \rightleftharpoons H_2O + H$	1.32	0.49	1.00	1.18	0.47	1.64	0.28	1.22	0.99
119. $HO_2 + OH \rightleftharpoons H_2O + O_2$	−0.02	−0.10	−0.10	−0.08	−0.03	−0.02	−0.02	−0.01	−0.01
128. $CO + OH \rightleftharpoons CO_2 + H$	0.00	0.00	0.00	0.00	0.00	0.00	−0.13	−0.93	−0.96

rate coefficient and the branching fraction instead of to the rate coefficients for each of the two product channels. Consequently, following Miller and Bowman[5] we consider k_T and α, rather than k_1 and k_2, to be independent parameters. Using the chain rule, sensitivity coefficients of NO for α and A_T, the temperature-independent factor in k_T, can be obtained from the raw sensitivity data. $\beta(A_T)$ and $\beta(\alpha)$ are then defined[5] as

$$\beta(A_T) = \frac{A_T}{X_{NO}} \frac{\partial X_{NO}}{\partial A_T}$$

$$\beta(\alpha) = \frac{\alpha}{X_{NO}} \frac{\partial X_{NO}}{\partial \alpha}$$

The sensitivity analysis shown in Table 3 confirms that the predicted NO concentration is controlled largely by the branching fraction α, while other parameters in the model, including the total rate k_T of the NH_2 + NO reaction, are less significant. Apart from α, the most sensitive parameters are the rate constants for reactions most important for radical generation, primarily those that consume or produce H atoms: $NH_3 + H \rightleftharpoons NH_2 + H_2$, $H + O_2 \rightleftharpoons OH + O$, $H + H_2O \rightleftharpoons OH + H_2$, and in the presence of CO, $CO + OH \rightleftharpoons CO_2 + H$. Because the rate coefficients for these reactions are known fairly accurately, their contribution to the uncertainty in α in the present analysis is limited.

The very large sensitivity to α of the initiation temperature predicted is illustrated further in Figure 3. Here the experimental data of sets 9 and 17 are compared to the model predictions with the optimum value of α as well as to those with α ± 0.1, using a simple AT^{β} expression to extrapolate α around the initiation temperature. The calculations shown were performed with a value of β of 1.9, consistent with the slope of the data on Figure 2, but variation of β between 0.5 and 2.0 provides the same trends. A change in α of 0.1 is seen to shift the initiation temperature more than 100 K for both experimental conditions. For comparison, the uncertainty in the measured temperature is less than 10 K.

Figure 3 shows that for the higher temperature set (set 9) the NO concentration decreases gradually from about 1270 K up to the selected initiation temperature of 1370 K. This behavior, typical of a number of the data sets, is not reproduced by the model, which predicts a steeper gradient in NO around the initiation temperature. The early reaction at very low conversions of NH_3 and NO is presently not well understood; it may involve amine/amine interactions or reactions at the quartz reactor walls.[6] However, at higher fractional conversion of the reactants (i.e. 10% and higher), these processes are no longer significant and the reaction is controlled largely by the NH_2 + NO branching fraction.

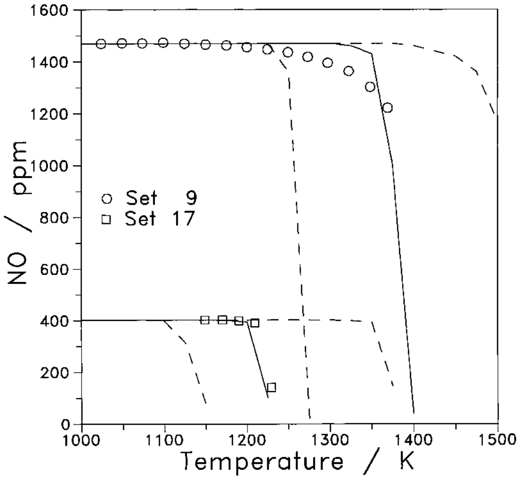

Figure 3. Comparison of experimental data and model predictions for the conditions of sets 9 and 17. Experimental data are shown as symbols, model predictions as solid lines and dashed lines, representing α and α ± 0.1, respectively.

As seen in Figure 2, the error bars for α are largest at the lower temperatures. To obtain reaction below 1300 K, it is necessary either to employ higher inlet concentrations of oxygen or to add carbon monoxide to the system to promote chain branching. In both cases the kinetics of the system become more complex, resulting in a somewhat increased uncertainty in our determination of α. However, it should be noted that the accumulated uncertainty in our determination of the branching fraction for the NH_2 + NO reaction is comparable to but not larger than the uncertainties reported for the direct high-temperature measurements.[11,13,15]

Figure 4 shows a summary of the reported data for the branching fraction of the NH_2 + NO reaction. The values of α obtained in the current work are in excellent agreement with data reported recently by Park and Lin[15] in the temperature range 302−1060 K. These two data sets indicate that the earlier measurements of Atakan et al.[11] and Stephens et al.[13] underestimated α in the 900−1200 K range. However, even though our data at the highest temperatures approach the values derived from flame studies,[31,32] they do not confirm the very sharp increase in branching fraction from 950 to 1200 K observed by Halbgewachs et al.[16]

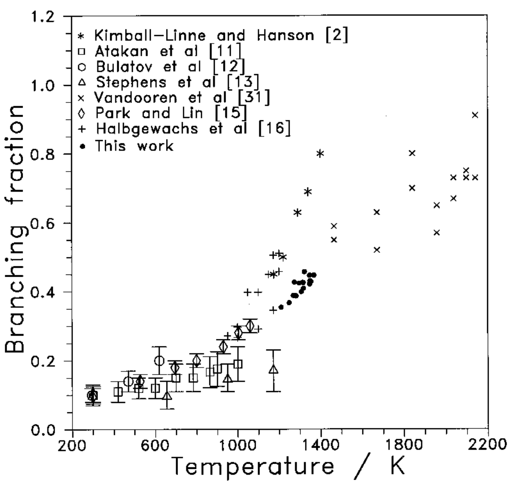

Figure 4. Summary of the results for the branching fraction α as function of temperature. For the direct measurements[11−13,15] error limits are shown for reference.

Conclusion

The branching fraction α of the NH_2 + NO reaction has been determined in the temperature range 1210−1370 K from flow reactor experiments on the $NH_3/NO/O_2$ and $CO/NH_3/NO/O_2$ systems. The experiments were carefully designed to minimize the impact of secondary reactions. The results show that α increases gradually from a value of 0.35 ± 0.04 at 1211 K to 0.45 ± 0.02 at 1369 K. The data blend smoothly with the most recent direct measurements of Park and Lin[15] and confirm the significant rise in branching fraction suggested by previous high-temperature determinations in static reactors and flames.

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