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Probing high-temperature amine chemistry: Is the reaction $\text{NH}_3 + \text{NH}_2 \rightleftharpoons \text{N}_2\text{H}_3 + \text{H}_2$ important?

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Abstract

The reaction $\text{NH}_3 + \text{NH}_2 \rightleftharpoons \text{N}_2\text{H}_3 + \text{H}_2$ (R1) has been identified as a key step to explain experimental results for pyrolysis and oxidation of ammonia. However, no direct experimental or theoretical evidence for the reaction has been reported. In the present work, the reaction was studied by ab initio theory and by re-interpretation of experimental data. We could not locate a transition state for R1 occurring as a direct process, but alternative mechanisms yielded an upper bound to k_1 of $1.5 \times 10^{13} \exp(-58.9 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ over 1000–2500 K, several orders of magnitude lower than values applied in modeling. Consistent with the theoretical work, re-evaluation of NH_3 pyrolysis data supported a very low value of k_1 . However, this finding opens up a novel unresolved issue. Current kinetic models cannot capture the NH_3 oxidation behavior in a number of laminar flow reactor and jet-stirred reactor experiments without adopting an improbably high value for k_1 . Important oxidation steps might be underestimated or missing from mechanisms.

Introduction

Ammonia is a carbon-free fuel and can be a suitable alternative for stationary power, transportation, and energy storage applications. Use of ammonia in engines is challenging, however, due to its poor combustion characteristics.¹⁻³ To improve the ability to predict ignition and oxidation of ammonia and thereby facilitate development of efficient combustion strategies for this difficult fuel, the combustion chemistry of NH₃ is investigated extensively. Recent kinetic models for ammonia oxidation include those of Mathieu and Petersen,⁴ Li et al.,⁵ Otomo et al.,⁶ Glarborg et al.,⁷ Mei et al.,^{8,9} Stagni et al.,¹⁰ and Jiang et al.¹¹ A number of these models were tested recently by Valera-Medina et al.³ who concluded that none of the tested mechanisms provided accurate predictions over a wider range of conditions. Even though ammonia is a comparatively simple molecule, its oxidation involves complexities not encountered for hydrocarbon fuels.

One of the current topics of discussion in the high temperature amine chemistry is the importance of the reaction,



This reaction was proposed by Dove and Nip¹² as a secondary step to explain the observed increased reactivity with reactant concentration in NH₃ pyrolysis in a shock tube. Subsequently, Konnov and De Ruyck¹³ showed that reaction R1 was consistent with the shock tube pyrolysis data of Davidson et al.,¹⁴ provided the pre-exponential factor for R1 estimated by Dove and Nip was lowered by a factor of 8. More recently, Alzueta and coworkers¹⁵⁻¹⁷ advocated the possible importance of R1 to explain flow reactor data for oxidation of NH₃. In their work, they adopted the rate constant from Dove and Nip,¹² but emphasized that an accurate determination of k_1 was desirable. Manna et al.,¹⁸ who studied oxidation of NH₃ with and without NO in a jet-stirred reactor, reported that using a value of k_1 twice as large as that estimated by Dove and Nip was required to explain the observed H₂ formation.

Other indirect support for reaction R1 came from the flow reactor study of Allen et al.¹⁹

on $\text{N}_2\text{O}/\text{H}_2$ mixtures. They detected formation of NH_3 and attributed it to the reaction sequence $\text{NH}_2 + \text{NH} (+\text{M}) \rightarrow \text{N}_2\text{H}_3 (+\text{M})$ (R2), $\text{N}_2\text{H}_3 + \text{H}_2 \rightarrow \text{NH}_3 + \text{NH}_2$ (R1b). Konov and De Ruyck²⁰ proposed a pathway to NO formation involving formation of N_2H_3 through the sequence $\text{N}_2 \xrightarrow{+\text{H}} \text{NNH} \xrightarrow{+\text{H}} \text{HNNH} \xrightarrow{+\text{H}} \text{N}_2\text{H}_3$, followed by $\text{N}_2\text{H}_3 + \text{H}_2 \rightarrow \text{NH}_3 + \text{NH}_2$ (R1b) and oxidation of NH_2 to NO. However, this NO forming pathway has not been confirmed by experiment.

There is no direct experimental or theoretical evidence for the reaction $\text{NH}_3 + \text{NH}_2 \rightleftharpoons \text{N}_2\text{H}_3 + \text{H}_2$. Consequently, in many recent modeling studies of NH_3 pyrolysis^{21,22} and combustion,⁴⁻¹¹ the reaction has been omitted from the mechanism. However, in other recent modeling work¹⁵⁻¹⁸ the reaction was included with a comparatively fast rate constant and had a significant impact on predictions. In practical applications such as engines, the ammonia concentration is much larger than in most laboratory experiments, augmenting the potential importance of this step. The purpose of the present work is to investigate the relevance of the $\text{NH}_3 + \text{NH}_2 \rightleftharpoons \text{N}_2\text{H}_3 + \text{H}_2$ reaction (R1). The reaction is studied by ab initio theory to provide an alternative estimate of its rate constant. Experiments conducted in shock tubes and flow reactors, relevant for the importance of R1, are re-interpreted in terms of the present value of k_1 and the practical implications of the findings are discussed.

Theory

Initial searches of the $2\text{N}/5\text{H}$ potential energy surface were made with B3LYP/6-311G(d,p) density functional theory. Despite application of several search algorithms (quadratic synchronous transit, coordinate driving and nudged elastic band) we were unable to locate a transition state (TS) for reaction R1 occurring as a direct process. An alternative mechanism might be addition/elimination via an N_2H_5 intermediate. A weakly bound $\text{H}_3\text{N}-\text{NH}_2$ species has been identified computationally by Hopper et al.²³ Our calculations indicate that it easily dissociates over a small barrier by breaking an N–H bond. While this leads

exothermically to $\text{H} + \text{N}_2\text{H}_4$ products, we find no further barrier to the migration of the H atom from the dissociating N–H bond towards a second N–H bond ultimately leading to more exothermic $\text{H}_2 + \text{N}_2\text{H}_3$ via a roaming mechanism. Metastable N_2H_5 and the TS for its dissociation were characterized as described in recent work on reaction pathways for N_2H_2 and N_2H_3 .²⁴ Geometries were obtained with the M06-2X density functional²⁵ combined with the 6-311++G(2df,2p) basis set,²⁶ also used for vibrational frequencies (scaled by factors of 0.970 and 0.945 for vibrational zero-point vibrational energy and partition functions,²⁷ respectively), and single-point energies were obtained via the CBS-APNO method²⁸ to approximate coupled cluster results at the complete basis set limit. Results obtained with the Gaussian program²⁹ are summarized in the Supplementary Material. Accuracy for N/H species has been demonstrated previously;²⁴ we note that here the computed $\Delta\text{H}(0\text{ K})$ for reaction 1 is $19.5\text{ kcal mol}^{-1}$ of the Active Thermochemical Tables value of $20.2\pm 0.2\text{ kcal mol}^{-1}$.³⁰

N_2H_5 is endothermic by $52.0\text{ kcal mol}^{-1}$ relative to $\text{NH}_3 + \text{NH}_2$ at 0 K and we assume collisions maintain a small equilibrium population which can dissociate over a further 0.6 kcal mol^{-1} barrier towards $\text{H} + \text{N}_2\text{H}_4$ and potentially $\text{H}_2 + \text{N}_2\text{H}_3$. An upper limit to the effective rate constant for reaction 1 is thus the product of the pre-equilibrium constant and high-pressure limit unimolecular rate constants. This is a limit because the extent of roaming, if any, is likely incomplete. We used the Multiwell program suite³¹ to evaluate these quantities, based on the rigid-rotor harmonic oscillator approximation. The low-barrier torsion around the N–N bond in N_2H_5 ($\sim 1.2\text{ kcal mol}^{-1}$) was treated as a sinusoidal potential. In the TS there is a single minimum for N–N torsion, which was treated as a vibration. In this way we set an upper bound to k_1 of $1.5\times 10^{13}\text{ exp}(-58.9\text{ kcal mol}^{-1}/\text{RT})\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$ over 1000–2500 K. Our calculated upper limit is compared to literature estimates in Fig. 1. We note that our value is very small, thanks to the high barrier, and even at 2500 K implies $k_1 < 1.1 \times 10^8\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$.

We have previously characterized the direct reaction $\text{N}_2\text{H}_4 + \text{H} \rightarrow \text{NH}_2 + \text{NH}_3$.³³ If, in

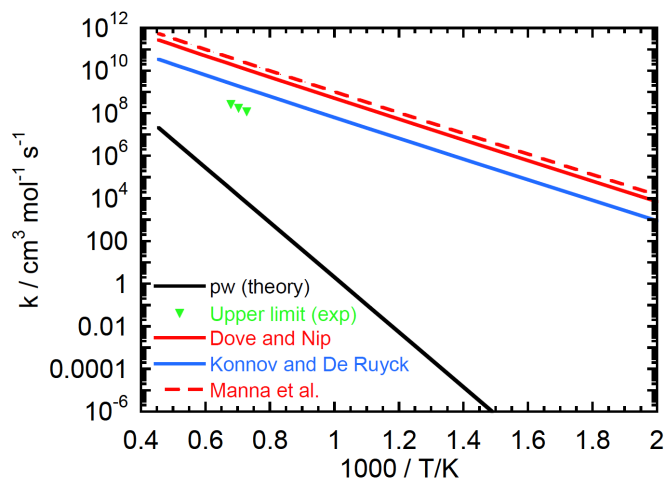


Figure 1: Arrhenius plot the reaction $\text{NH}_3 + \text{NH}_2 \rightleftharpoons \text{N}_2\text{H}_3 + \text{H}_2$ (R1). The present calculated value, which we assume to be an upper limit, is compared to estimates from Dove and Nip,¹² Konnov and De Ruyck,¹³ and Manna et al.¹⁸ Also shown is upper limit values derived from modeling the flow reactor results of Benes et al.,³² as discussed below.

the reverse direction, some trajectories over the TS lead to roaming of the H atom near N_2H_4 , then we speculate that $\text{H}_2 + \text{N}_2\text{H}_3$ could be formed. Combination of the $\text{N}_2\text{H}_4 + \text{H}$ barrier with the reaction enthalpy implies a vibrationally adiabatic energy barrier for the reverse $\text{NH}_2 + \text{NH}_3 \rightarrow \text{N}_2\text{H}_4 + \text{H}$ of $53.4 \text{ kcal mol}^{-1}$,³³ similar to that for the addition/elimination pathway. Reversing $\text{N}_2\text{H}_4 + \text{H} \rightarrow \text{NH}_2 + \text{NH}_3$ via the equilibrium constant and with the clearly excessive assumption that every trajectory leads to H_2 formation by roaming yields an upper limit for $\text{NH}_2 + \text{NH}_3 \rightarrow \text{H}_2 + \text{N}_2\text{H}_3$ of $1.3 \times 10^{13} \exp(-58.8 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ over 1000–2500 K for this more direct mechanism; the value is almost identical to the one obtained for the addition-elimination mechanism.

Kinetic Modeling

In this section, selected published experiments, relevant for the importance of R1, are re-interpreted. The experiments were conducted in shock tubes, flow reactors, and jet-stirred reactors, and include data for NH_3 pyrolysis,^{12,14,21,32} NH_3 oxidation,¹⁵ and $\text{N}_2\text{O}/\text{H}_2$ mixtures.¹⁹ The chemical kinetic model used in the simulations was adopted from Glarborg.³⁴ It

was based mainly on the review of nitrogen chemistry by Glarborg et al.,⁷ but with modifications based on more recent studies, including work on $\text{NH}_2 + \text{H} (+\text{M})$,^{22,35} $\text{NH}_3 + \text{HO}_2$,¹⁰ $\text{NH}_2 + \text{HO}_2$,^{35,36} $\text{NH}_2 + \text{NO}_2$,³⁴ as well as steps in the diazene subset.²⁴

NH₃ pyrolysis

Ammonia pyrolysis in shock tubes has been studied by a number of groups.^{12,14,21,37-44} The shock tube results selected for analysis were chosen mostly because they had been used in the past to justify the existence of R1. However, we have also included the results of Alturaifi et al.²¹ in the analysis since they are more reliable than most of the older studies.

Dove and Nip¹² investigated the pyrolysis of ammonia in a shock tube over a range of temperature and starting NH_3 concentration, with Kr as inert gas. They extracted gas from the shock tube and measured concentrations of selected species by mass spectrometry. Based on a kinetic interpretation of their measurements, they estimated the rate constant for $\text{NH}_3 + \text{NH}_2 \rightleftharpoons \text{N}_2\text{H}_3 + \text{H}_2$. Dove and Nip observed that the NH_3 decomposition rate increased by a factor of three when the starting concentration of NH_3 was increased from 0.14% to 6.2%. They attributed this effect to the impact of secondary reactions, in particular $\text{NH}_3 + \text{NH}_2$ (R1). Their findings on the $\text{NH}_3 + \text{NH}_2$ reaction must be interpreted with caution, however. At the time of their study (1979), the knowledge of the secondary chemistry of ammonia pyrolysis was rudimentary and this limitation affected their kinetic interpretation. For example, at 1700 K the kinetics for $\text{H} + \text{NH}_3 \rightarrow \text{H}_2 + \text{NH}_2$ measured directly by Michael et al.⁴⁵ are 10 times faster than derived by Dove and Nip. Furthermore, probing of reaction progress behind shock waves with time-of-flight mass spectrometry could be difficult due to boundary layer effects.⁴⁶

Figure 2 compares the measurements of Dove and Nip¹² at the high NH_3 level (6.2%) and 2511 K with modeling predictions with the present mechanism, investigating the impact of the value of k_1 . Calculations are shown for the calculated upper limit of k_1 from the present work, as well as for values from Dove and Nip¹² and Konnov and De Ruyck.¹³

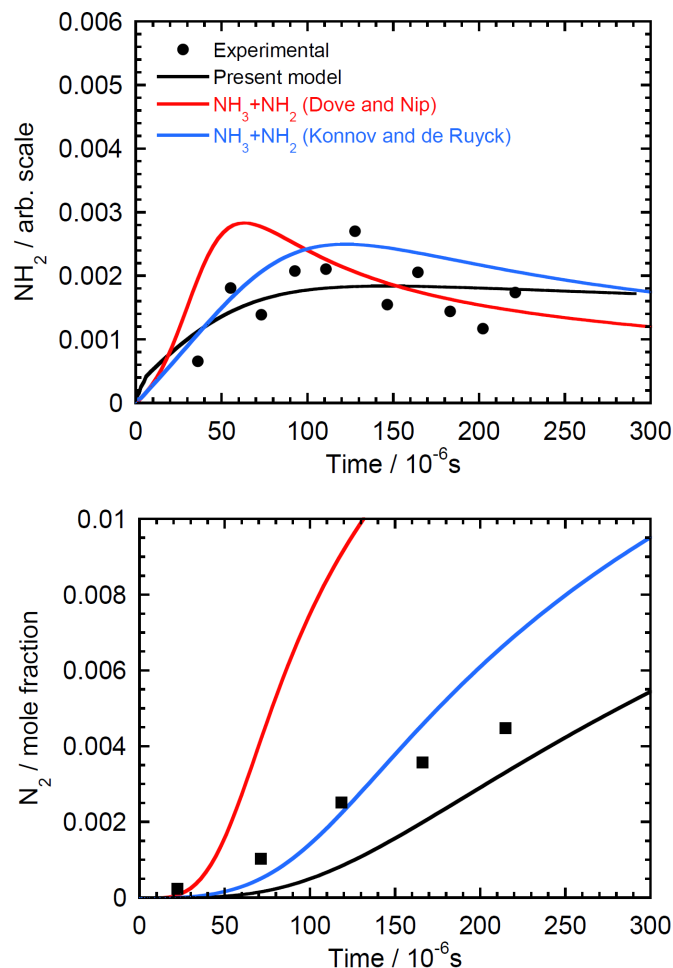


Figure 2: Comparison of the shock tube measurements of Dove and Nip¹² and modeling predictions for formation of NH_2 (upper, figure, arbitrary scale) and N_2 (lower figure) in decomposition of NH_3 . Experimental conditions: 6.2% NH_3 in Kr at 0.35 atm and 2511 K.

The data obtained for NH_2 (upper figure) were relative measurements and have been scaled to the modeling predictions. The predicted NH_2 profile depends on the choice of k_1 , with a slightly better agreement within the scatter of the measurements obtained with the values of k_1 from Konnov and De Ruyck and from the present work. For N_2 (lower figure, absolute measurement), the predictions are even more sensitive to the rate constant for R1. The best prediction of the time for onset of N_2 formation is obtained with the Konnov and De Ruyck value for k_1 , while the formation rate upon initiation is calculated more accurately

with the present value. Conceivably, uncertainties in the N₂-amine chemistry^{24,33,46} could have a significant impact on the predicted N₂ profile. However, the predictions do not support the large rate constant estimated by Dove and Nip, which results in a significant overprediction of N₂.

The increased consumption rate for NH₃ observed by Dove and Nip at a high concentration of NH₃ can partly be attributed to different secondary reactions. However, the most important factor is possibly the enhanced collision efficiency of NH₃ compared to Kr for thermal dissociation of NH₃. Dove and Nip estimated that a factor of 40 could explain the observed increase in consumption rate for NH₃. Glarborg et al.³⁵ calculated that the relative third body efficiency of NH₃ compared to Ar is approximately 22 at 2000 K; Kr would be expected to have a collision efficiency broadly similar to Ar.

Davidson et al.¹⁴ measured NH₂ and NH profiles in NH₃ decomposition under more dilute conditions, but in the same temperature range as Dove and Nip. Konnov and De Ruyck¹³ interpreted the data in terms of their kinetic model. They found some support for the NH₃ + NH₂ reaction, but decreased the rate constant by a factor of 8 compared to the evaluation of Dove and Nip.¹² Recently, Glarborg et al.²² re-interpreted the results from Davidson et al. and concluded that the data did not provide evidence for the existence of reaction R1.

Figure 3 compares the measured NH₂ at 2300 K with modeling predictions. The early profile of NH₂ and the peak concentration are captured well by the present model, but the NH₂ consumption rate at longer times is underpredicted. Adoption of the rate constant for R1 from Konnov and De Ruyck improves slightly on the accuracy of the prediction, but the difference is too small to define k_1 due to uncertainties in the secondary amine chemistry. However, use of the value of k_1 from Dove and Nip results in a formation rate of NH₂ that is too fast compared to experiment; supporting the conclusion of Konnov and De Ruyck.

Alturaifi et al.²¹ monitored the NH₃ decay as a function of time in shock tube experiments with initial concentrations of ammonia of about 0.5%. Figure 4 compares their measurements

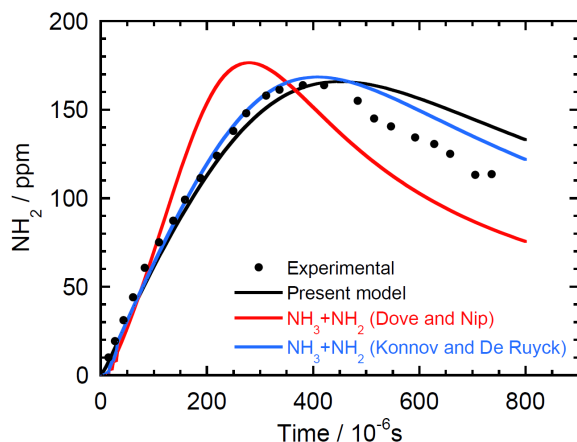


Figure 3: Comparison of the shock tube measurements of NH_2 and NH by Davidson et al.¹⁴ with modeling predictions in decomposition of NH_3 at about 2300 K. Experimental conditions: 0.27% NH_3 in Ar at 1.028 atm and 2301 K.

with modeling predictions for a temperature of 2096 K. The prediction with the present value of k_1 is seen to capture the measurements well, while the larger rate constants of Konnov and De Ruyck and, especially, Dove and Nip are not supported by the experiment. This is consistent with the analysis of Alturaifi et al., who did not include reaction R1 in their mechanism.

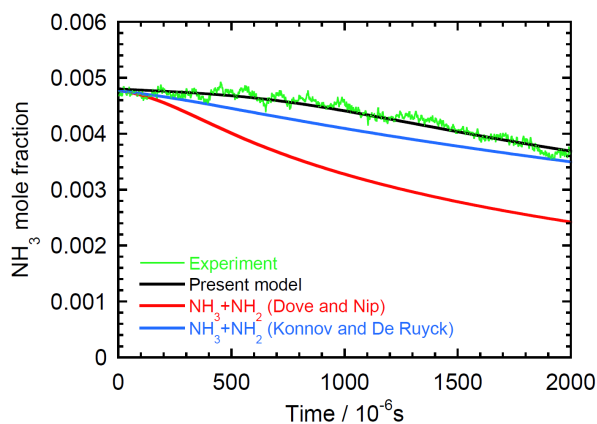


Figure 4: Comparison of the shock tube measurements of NH_3 by Alturaifi et al.²¹ with modeling predictions for decomposition of ammonia. Experimental conditions: 0.48% NH_3 in Ar at 2096 K and 1.25 atm.

Benes et al.³² did a comprehensive experimental study of the pyrolysis of NH_3 in a flow

reactor, varying the inlet concentration, temperature, and residence time. Figure 5 compares measured NH_3 consumption profiles as a function of temperature with modeling predictions. The results show that the rate constant for the $\text{NH}_3 + \text{NH}_2$ reaction (R1) has a strong impact on the modeling predictions. Use of the present value of k_1 results in underprediction of the NH_3 decomposition rate. Contrary to this, modeling with the proposed rate constants from Konnov and De Ruyck¹³ and Dove and Nip¹² causes a significant overprediction of the NH_3 consumption rate.

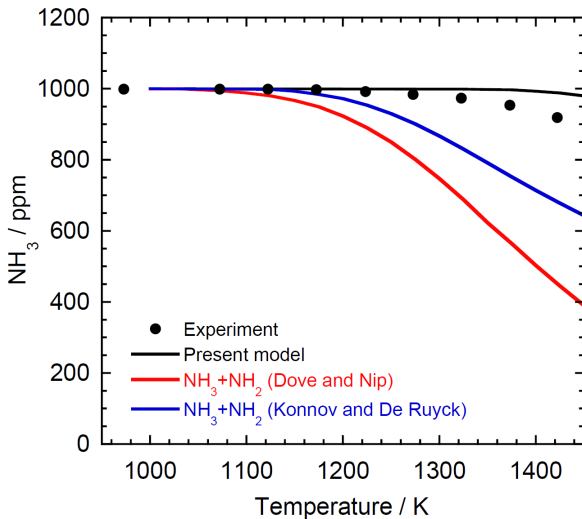


Figure 5: Comparison of the flow reactor measurements of NH_3 by Benes et al.³² with modeling predictions in decomposition of NH_3 temperatures in the range 1322-1472 K. Experimental conditions: ~ 1000 ppm NH_3 in Ar at atmospheric pressure. The experiments were conducted in a quartz reactor. The residence time (s) was $4119/T(\text{K})$.

The present model provides fairly accurate predictions of ammonia pyrolysis under shock tube conditions,²² but fails to capture the ammonia decomposition in the flow reactor, as seen in Fig. 5. The discrepancy may be caused by short-comings in the mechanism. The kinetic model of Alturaifi et al.²¹ provides a much better agreement with the flow reactor data, indicating that the underprediction of the ammonia decomposition rate may be a result of uncertainties in the present reaction mechanism. However, heterogeneous chemistry on

the quartz reactor wall may also play a role. Manna et al.⁴⁷ investigated NH_3 pyrolysis in laminar flow reactor made of either quartz or alumina, with and without addition of water vapor, to evaluate possible surface effects. They concluded that surface decomposition of NH_3 was important under inert conditions, where significant amounts of H_2 and N_2 were formed above 1000 K.

Figure 6 shows results for the NH_3 consumption profiles as a function of time for selected temperatures. Calculations are shown only for the values of k_1 from Dove and Nip (upper) and Konnov and De Ruyck (lower). Use of either of the two rate constants results in a strong overprediction of the decomposition rate of NH_3 . Since R1 involves reaction between the reactant and its derived radical, uncertainties in the secondary chemistry cannot explain the discrepancy.

The results of Benes et al. provide experimental evidence that the rate constant for the $\text{NH}_3 + \text{NH}_2$ reaction (R1) must be lower than the values proposed by Dove and Nip and Konnov and De Ruyck, respectively. Based on kinetic modeling of the flow reactor data, estimated upper limit values of k_1 can be derived for temperatures of 1372, 1422 and 1472 K. These values, shown as green symbols in Fig. 1, are roughly an order of magnitude below the rate constant estimated by Konnov and De Ruyck.

NH_3 oxidation

Abian et al.¹⁵ studied ammonia oxidation in an atmospheric pressure flow reactor at comparatively low O_2 levels and temperatures in the range 850-1450 K. They found that the kinetic models of Glarborg et al.⁷ and Stagni et al.¹⁰ greatly underpredicted the consumption rate for NH_3 . Including the $\text{NH}_3 + \text{NH}_2$ reaction in the mechanism improved the agreement with experiment; the best overall modeling predictions were obtained with the rate constant from Dove and Nip.¹² Abian et al. concluded that a reliable determination of k_1 was desirable.

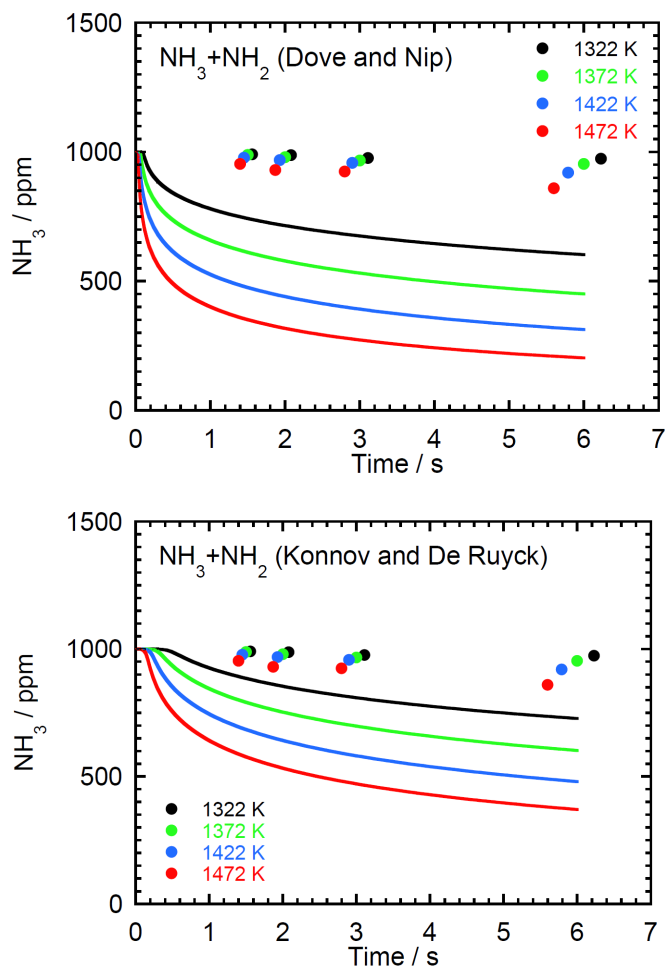


Figure 6: Comparison of the flow reactor measurements of NH_3 by Benes et al.³² with modeling predictions in decomposition of NH_3 for selected temperatures in the range 1322-1472 K. Experimental conditions: ~ 1000 ppm NH_3 in Ar at atmospheric pressure.

Figure 7 compares selected experimental results from Abian et al. with modeling predictions. Similar to the kinetic models of Glarborg et al.⁷ and Stagni et al.,¹⁰ the present model strongly underpredicts the consumption of NH_3 . In line with the findings of Abian et al., inclusion of R1 with a comparatively fast rate constant (from Konnov and De Ruyck or from Dove and Nip) is seen to enhance significantly the reactivity of the model. However, the shape of the predicted NH_3 profile is not consistent with experiment. While a high value of k_1 improves the prediction of the initiation temperature, it also leads to overprediction of the consumption rate of NH_3 after initiation.

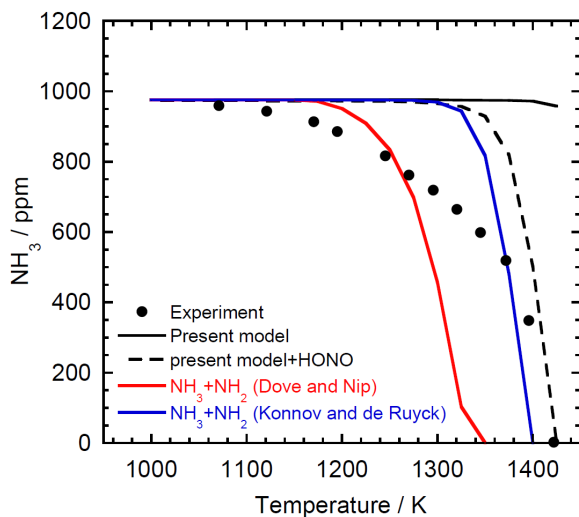


Figure 7: Comparison of the flow reactor measurements of NH_3 by Abian et al.¹⁵ with modeling predictions in oxidation of NH_3 . Experimental conditions: 976 ppm NH_3 , 780 ppm O_2 ; balance N_2 . Pressure is atmospheric and the residence time (s) in the isothermal zone is $195/T(\text{K})$.

Ammonia oxidation in laminar flow quartz reactors may be initiated by surface reactions.^{7,48} The mechanism of initiation is not known, but conceivably a reactive intermediate is formed on the reactor surface, followed by desorption into the gas phase. Following Glarborg,³⁴ we assess the potential importance of this phenomenon by introducing 1 ppm of HONO in the reactant mixture in the modeling. The resulting calculation, shown as a dashed line in Fig. 7, indicates that surface initiation may indeed be important under these conditions. The initiation temperature is lowered by perhaps 100 K and the predicted NH_3 profile becomes similar to that obtained by adopting the rate constant for R1 from Konnov and De Ruyck. However, the failure of the model to capture the observed results persists. Recently, Alzueta et al.⁴⁹ reported similar discrepancies for oxidation of CO/NH_3 mixtures in a quartz reactor at low O_2 . More work is desirable to resolve this issue.

In addition to the pyrolysis work discussed above, Manna et al.⁴⁷ investigated NH_3 oxidation in both a laminar flow reactor and a jet-stirred reactor. Also for oxidizing conditions, they evaluated the impact of surface effects, concluding that heterogeneous reactions were

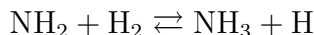
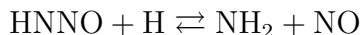
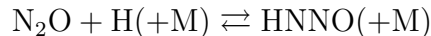
less important in the presence of O_2 . In a more recent study, Manna and coworkers¹⁸ reported results for oxidation of NH_3 in a jet-stirred reactor in the absence and presence of NO . They observed formation of H_2 above 1000 K. Modeling predictions with literature mechanisms strongly underpredicted the H_2 yield. However, inclusion of the $NH_3 + NH_2$ reaction (R1) with a very high rate constant (twice the value from Dove and Nip), improved the accuracy of the predictions significantly.

Since the present work provides support for a much lower value of k_1 , the cause of the discrepancy should be found elsewhere. It can be attributed to short-comings of the kinetic models or to experimental artifacts. The jet-stirred reactor design used by Manna and coworkers was described in more detail by Lavadera et al.⁵⁰ The main flow (O_2 and inert) and a secondary flow (fuel and inert) are mixed in a premixing chamber (with a very small volume compared to the JSR) and then fed to the jet-stirred reactor. The main flow is preheated in a quartz tube to the reactor temperature prior to mixing. If also the secondary flow is preheated, a fraction of the NH_3 may decompose on the tube surface during preheating, resulting in H_2 formation. The observed H_2 yield in the experiments of Manna et al.¹⁸ was independent of the presence of NO . The $NH_2 + NO$ reaction is known to affect strongly the generation of chain carriers in the $NH_3/O_2/NO$ system.⁷ Even though the experiments were conducted at high NH_3/NO ratios, this could be an indication that the H_2 formation was not strongly dependent on the radical pool. Either way, more work is required to resolve the observed discrepancies between experiment and modeling.

The N_2O/H_2 reaction in a flow reactor

Allen et al.¹⁹ investigated oxidation of N_2O/H_2 mixtures in a flow reactor at 995 K and 3 atm. In addition to monitoring N_2O and H_2 , they detected NH_3 as a minor intermediate. Allen et al. proposed that the NH_3 formation resulted mainly from the sequence $NH_2 + NH (+M) \rightarrow N_2H_3 (+M)$, $N_2H_3 + H_2 \rightarrow NH_3 + NH_2$. However, the theoretical work of Klippenstein et al.⁵¹ on $NH_2 + NH$ does not support stabilization of N_2H_3 ; the reaction yields mostly $HNNH$

+ H. Furthermore, according to the present work the $\text{N}_2\text{H}_3 + \text{H}_2 \rightleftharpoons \text{NH}_3 + \text{NH}_2$ reaction is very slow. We attribute the formation of NH_3 mostly to an alternative mechanism involving HNNO,



This sequence of reactions is plausible, as theoretical work supports some stabilization of HNNO from the $\text{N}_2\text{O} + \text{H}$ reaction at low to intermediates temperature.⁵² However, to facilitate quantitative predictions, more work is required on the thermochemistry and reaction subset of HNNO.

Concluding remarks

The initial experiments that led to the proposal of reaction R1 as a way to account for the faster loss of NH_3 at high temperatures as its initial concentration was raised are shown, in hindsight, to be interpretable with an extremely slow, essentially negligible, value of k_1 . Reinterpretation of some other pyrolysis observations indicates reasonable agreement with experiment can be obtained when $k_1 \sim 0$. In particular, the flow reactor pyrolysis data of Benes et al.³² seem to be incompatible with a fast rate for R1. However, direct experimental measurement of R1 or discovery through quantum calculations of a pathway more favorable than those identified here would support further consideration of the reactivity via R1.

Analysis of some more complicated oxidation experiments leaves open the possible contribution of R1 in these contexts, although, based on the present findings, it is likely that R1 is to some extent partly accounting for unknown oxidation steps that have not been incorporated into present mechanisms. It is important to clarify why current kinetic models cannot capture the NH_3 oxidation behavior in a number of laminar flow reactor and

jet-stirred reactor experiments without adopting an improbably high value for k_1 .

Supporting Information for Publication

Structures, Cartesian coordinates, vibrational frequencies, and computed energies. Reaction mechanism and thermodynamic data for modeling.

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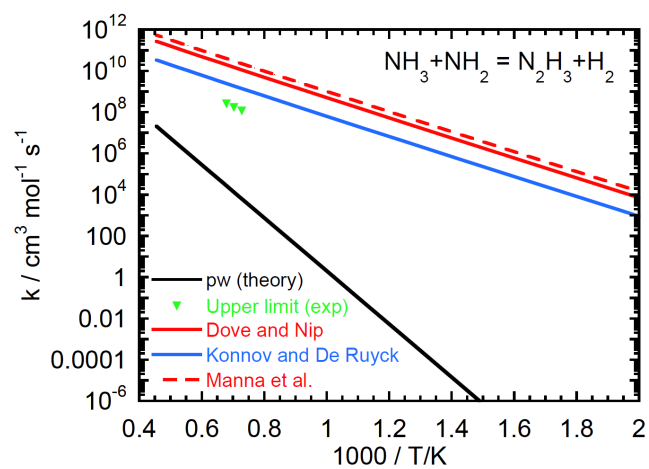


Figure 8: TOC graphic