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Ammonia Oxidation at High Pressure and Intermediate Temperatures

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Keywords: NH$_3$ oxidation, high pressure, flow reactor, H$_2$NO + O$_2$ rate constant, kinetic model

Ammonia oxidation experiments were conducted at high pressure (30 bar and 100 bar) under oxidizing and stoichiometric conditions, respectively, and temperatures ranging from 450 to 925 K. The oxidation of ammonia was slow under stoichiometric conditions in the temperature range investigated. Under oxidizing conditions the onset temperature for reaction was 850-875 K at 30 bar, while at 100 bar it was about 800 K, with complete consumption of NH$_3$ at 875 K. The products of reaction were N$_2$ and N$_2$O, while NO and NO$_2$ concentrations were below the detection limit even under oxidizing conditions. The data were interpreted in terms of a detailed chemical kinetic model. The rate constant for the reaction of the important intermediate H$_2$NO with O$_2$ was determined from ab initio calculations to be 2.3 x $10^2$
$T^{2.994} \exp(-9510 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The agreement between experimental results and model work was satisfactory. The main oxidation path for NH$_3$ at high pressure under oxidizing conditions is \[ \text{NH}_3 \xrightarrow{+\text{OH}} \text{NH}_2 \xrightarrow{+\text{HO}_2} \text{NO}_2 \xrightarrow{+\text{O}_2} \text{HNO} \xrightarrow{+\text{O}_2} \text{NO} \xrightarrow{+\text{NH}_2} \text{N}_2. \] The modeling predictions are most sensitive to the reactions \( \text{NH}_2 + \text{NO} = \text{NNH} + \text{OH} \) and \( \text{NH}_2 + \text{HO}_2 = \text{H}_2\text{NO} + \text{OH} \), which promote the ammonia consumption by forming OH radicals, and to \( \text{NH}_2 + \text{NO} = \text{N}_2 + \text{H}_2\text{O} \) and \( \text{NH}_2 + \text{NO}_2 = \text{N}_2\text{O} + \text{H}_2\text{O} \), which are the main chain-terminating steps.

**Introduction**

Ammonia is an important combustion intermediate in formation of nitric oxide from nitrogen organically bound in fuels. For most solid fuels, NH$_3$ is formed directly during devolatilization [1], and it has also been reported as a product of gasification [2]. The selectivity for forming NO or N$_2$ from N-volatiles in combustion depends largely on the fate of amine radicals such as NH$_2$, NH, and N [1,3]. Ammonia is also known as an efficient additive for Selective Non-Catalytic Reduction of NO (SNCR) [3,4]. Recently, ammonia has attracted interest as a potential carbon-free energy carrier [5]. Results on oxidation of NH$_3$ are available from flames [6–16], shock tubes [17–27], and flow reactors [2,28–30]. In addition, a number of modeling studies and reviews of ammonia chemistry have been reported [3,27,28,31–35]. Supplementing the oxidation studies, extensive work has been conducted on the kinetics of the SNCR process [3,4,36–38].

With the interest in amine-based fuels as energy carriers [39], reliable experimental data for oxidation of ammonia at high pressure become important.
High-temperature results at increased pressure are available from recent work in shock tubes and premixed flames. Mathieu and Petersen [27] measured the ignition time for ammonia diluted in Ar at 1.4, 11, and 30 bar, respectively, while Hayakawa et al. [15] determined the burning velocity of ammonia/air mixtures at pressures of 1-5 bar. However, studies of ammonia oxidation at low-to-medium temperatures and high pressure are scarce.

The purpose of the present study is to investigate ammonia oxidation at high pressure (30-100 bar) and temperatures up to 925 K. Experiments are conducted with stoichiometric and lean NH$_3$/O$_2$ mixtures, highly diluted in N$_2$, in a laminar flow reactor. The results are interpreted in terms of a detailed chemical kinetic model for ammonia oxidation. The reaction mechanism, which is based on earlier work on nitrogen chemistry [34, 38, 40, 41], is updated in the present work, emphasizing reactions important at high pressure. Under the present conditions, the nitroxide radical H$_2$NO is an important intermediate, and the rate constant for the reaction between H$_2$NO and O$_2$ has been derived from ab initio calculations.

**Experimental**

The experimental setup was a laboratory-scale high-pressure laminar flow reactor designed to approximate plug flow. The setup is described in detail elsewhere [42] and only a brief description is provided here. The system was used here for investigation of ammonia oxidation at 30 bar and 100 bar pressure, respectively, and temperatures from 450 to 925 K. The reactant gases were premixed before entering the reactor. The reactions took place in a tubular tube under laminar flow conditions. The tube was made of quartz
(inner diameter of 7.5 mm) or alumina (Degussit AL23, inner diameter 6 mm). The temperature profile in the flow reactor was measured by a thermocouple positioned in the void between the quartz reactor and the steel shell. Results for 100 bar are shown in Fig. 1 while the 50 bar profiles are available as supplementary material. An isothermal reaction zone of 39-47 cm was achieved in the reactor. All gases used in the present experiments were high purity gases or mixtures with certified concentrations. The total flow rate was 2.8 L min⁻¹ (STP). The product analysis was conducted with an on-line 6890N Agilent Gas Chromatograph (GC-TCD/FID from Agilent Technologies) and an AO2020 NH₃/NO/NO₂ analyser from ABB. The relative measurement uncertainties for the species detected were in the range ±2-6%.

**Chemical Kinetic Model**

The starting mechanism and corresponding thermodynamic properties were drawn from the recent work by Klippenstein et al. [38]. The mechanism was carefully updated, emphasizing reactions of importance under the conditions of the present study. Table 1 lists the key reactions in the NH₃ oxidation scheme with the rate coefficients used in the present work. The full mechanism is available as supplemental material.

At the high-pressure medium-temperature conditions of this work, ammonia oxidation occurs to a significant extent through the H₂NO intermediate. Rate constants for H₂NO reactions are generally quite uncertain. In the present work, we characterize the key reaction of H₂NO with O₂ by ab initio calculations, as described below.
**Ab initio calculations**

The nitroxide radical H$_2$NO, molecular oxygen and the transition state for their reaction were investigated computationally. First, geometries and frequencies (scaled by a standard factor of 0.954 [54]) were obtained with UQCISD/6-311G(d,p) theory, using spin-unrestricted wavefunctions as implemented within the Gaussian 09 code [55]. At these geometries (see Fig. 2), single-point energies were calculated at the UCCSD(T) level of theory with the aug-cc-pVTZ and aug-cc-pVQZ basis sets, using spin-restricted wavefunctions within the Molpro 2010 program [56], and extrapolated to the complete basis set limit for coupled cluster theory (CCSD(T)/CBS). Corrections were added to this result based on UCCSD(T)/cc-pwVTZ results obtained with core electrons included and excluded from the correlation treatment, and relativistic effects evaluated at the CISD/cc-pwVTZ level of theory. The results are summarized in the supplementary material. The rate constant was then derived via canonical transition state theory as implemented within the Multiwell program suite [57], with tunneling accounted for via the Eckart model.

Some of the prior studies of H$_2$NO raised the issue of whether this molecule is planar or pyramidal [58, 59]. Out-of-plane bending of the C$_{2v}$ structure was explored via scans of the angle between the O-N bond and the NH$_2$ plane, with the rest of the geometry allowed to optimize. The results are plotted in Fig. 3 that shows a double well potential with a very small barrier of 17 cm$^{-1}$ to inversion. The harmonic frequency evaluated at either minimum is 481 cm$^{-1}$, but clearly the potential is significantly anharmonic. The moment of inertia for bending was estimated to be 0.407 amu Å$^2$, by treating the planar geometry like a three-atom linear molecule [60] with a mass of 2 amu.
at the midpoint of the two H atoms. The eigenvalues obtained via the FGH method [61] for quantized bending motion on this potential are summarized in the supplemental material; the first three are 142, 508 and 1030 cm\(^{-1}\) above the minima. Even the lowest level is well above the inversion barrier so H\(_2\)NO explores both sides equally. Because the wavefunction for the ground state is maximized at the planar geometry, we use this structure and a symmetry number of 2 to calculate rotational partition functions. Vibrational partitions were based on the harmonic oscillator model for the remaining 5 modes of H\(_2\)NO combined with results derived via a direct count for the out-of-plane bending energy levels. Together with the heat of formation at 298 K from the Active Thermochemical Tables [62], the thermochemistry is summarized within the NASA polynomial included in the supplemental information.

**Reaction mechanism**

The reactions of ammonia with the radical pool and O\(_2\) involve hydrogen abstraction to form NH\(_2\). The rate constants for these steps, taken from the mechanism of Klippenstein et al. [38], are mostly well established, but the values for NH\(_3\) + HO\(_2\) (R4) (estimated [3]) and NH\(_3\) + O\(_2\) (R5b) (ab initio calculation [47]) are more uncertain.

The oxidation rate for ammonia and the products of reaction are largely determined by the fate of NH\(_2\). The NH\(_2\) radical is mainly consumed by reaction with the HO\(_2\) radical (R5b, R11-R13), which builds up in considerable concentrations under the present conditions, and with the stable species NO (R18, R19) and NO\(_2\) (R20, R21). The NH\(_2\) + HO\(_2\) reaction has been studied theoretically by several groups [33,47,63-65], while there
are only indirect room temperature measurements available for the rate constant [66–68]. It has a number of product channels and may occur both on the singlet and triplet surfaces. We choose to rely on the work of Sumathi and Peyerimhoff [47] who calculated rate constants for formation of the adduct H$_2$NOOH and its isomers HN(OH)OH and H$_2$N(OH)O, as well as the products NH$_3$ + O$_2$, NH$_2$O + OH, HNO + H$_2$O, and HON + H$_2$O. The predominant contribution to the total rate constant is predicted to be dissociation of energized H$_2$NOOH to NH$_2$O + OH over the temperature range 300–2000 K and pressures from 0.001 to 10 atm. At pressures above 10 atm, stabilisation of H$_2$NOOH becomes important according to Sumathi and Peyerimhoff. However, little is known about the fate of the H$_2$NOOH adduct. In the present work, we take H$_2$NO + OH (R11) to be the primary products of reaction and assume the rate constant to be equal to the high-pressure limit of the overall reaction, which we estimate to 5 × 10$^{13}$ cm$^3$ mol$^{-1}$ s$^{-1}$. This value is only slightly higher than the indirect measurement for NH$_2$ + HO$_2$ by Lozovskii et al. [67] at 570 torr, but a factor of two higher than the calculation of Sumathi and Peyerimhoff.

The rate constants for the reactions of NH$_2$ with NO and NO$_2$,

\begin{align*}
\text{NH}_2 + \text{NO} &\rightleftharpoons \text{N}_2 + \text{H}_2\text{O} \\
\text{NH}_2 + \text{NO} &\rightleftharpoons \text{NNH} + \text{OH} \\
\text{NH}_2 + \text{NO}_2 &\rightleftharpoons \text{N}_2\text{O} + \text{H}_2\text{O} \\
\text{NH}_2 + \text{NO}_2 &\rightleftharpoons \text{H}_2\text{NO} + \text{NO}
\end{align*}

have been discussed in detail in recent work by Klippenstein and coworkers [38, 51]. We have adopted their values without modifications. For NH$_2$ + NO$_2$, formation of the adducts H$_2$NNO$_2$ and H$_2$NONO is pressure dependent,
but Klippenstein et al. predict little effect of pressure below 100 atm because the complex lifetimes are too short to permit significant collisional relaxation [51].

Nitrooxide may be formed in significant quantities from reaction of \( \text{NH}_2 \) with \( \text{HO}_2 \) and \( \text{NO}_2 \). The \( \text{H}_2\text{NO} \) subset of the reaction mechanism consists largely of reactions with estimated rate constants. While the most important reaction of \( \text{H}_2\text{NO} \) is that with \( \text{O}_2 \), discussed above, also the reactions with \( \text{HO}_2 \) (R28) and \( \text{NH}_2 \) (R30) are important consumption steps. The value of \( k_{28} \) is a rough estimate [36] and \( k_{30} \) was derived from QRRK calculations [33]. Similarly to \( \text{H}_2\text{NO} \), \( \text{HNO} \) is mostly consumed by reaction with \( \text{O}_2 \) (R32); also for this step we use a rate constant based on QRRK theory [33].

**Results and discussion**

Experiments for \( \text{NH}_3 \) oxidation with high dilution in \( \text{N}_2 \) as a function of temperature from 450 K to 900 K were conducted under stoichiometric and oxidizing conditions. Table 2 lists the experimental conditions. The fuel-air equivalence ratio, defined from the overall reaction \( \text{NH}_3 + 1.25\text{O}_2 \rightarrow \text{NO} + 1.5\text{H}_2\text{O} \), ranged from approximately 1.0 to 0.02. Simulations with the full temperature profile were conducted using the CHEMKIN PRO software package [69]. Calculations restricted to the isothermal zone of the reactor showed similar trends, but with a smaller conversion at the highest temperatures (oxidizing conditions). The experimental results are compared with modeling predictions in Figs. 4-7. Symbols denote the experimental data and lines denote numerical results.
Figures 4 and 5 show results for NH$_3$ oxidation under stoichiometric conditions and pressures of 30 and 100 bar, respectively. At 30 bar the onset of reaction occurs at 800 K. However, even above this temperature consumption of NH$_3$ is very slow; at 925 K 730 ppm NH$_3$ (95% of the inlet concentration) and about 900 ppm O$_2$ (97% of the inlet concentration) are still unreacted in the reactor outlet. At 100 bar, NH$_3$ consumption also starts around 800 K, but as the temperature increases oxidation is slightly faster than at 30 bar. This can partly be attributed to a longer residence time. However, at 900 K still 675 ppm NH$_3$ (i.e., 95% of the inlet) remains unreacted.

The modeling results for stoichiometric conditions at 30 bar and 100 bar show very little reaction. The agreement with experiment can be considered satisfactory, since the measurements show that only around 40 ppm or about 5% of NH$_3$ are consumed at the highest temperatures at the two pressures.

Figure 6 shows the results for NH$_3$ oxidation at 30 bar for fuel-lean conditions. To investigate the impact of surface effects, these experiments were conducted in both an alumina and a quartz tube. Ammonia is known to decompose on quartz surfaces [70–72], and while surface effects are unimportant in SNCR for experiments carried out at low surface-to-volume ratios [36,73], it has been observed that induction times for oxidation of NH$_3$ in quartz reactors were influenced by heterogeneous effects [28].

In the figure, the closed symbols indicate experimental results obtained in the quartz tube, while the open symbols denote results from the alumina tube. In the quartz tube, the onset temperature for reaction occurs at 850 K, compared to a value of 875 K observed in the alumina tube. The difference can partly be attributed to the longer residence time in the quartz reactor, but it cannot be ruled out that some surface initiation takes place in the
quartz reactor, despite the high pressure.

Upon initiation, NH$_3$ is oxidized to N$_2$ (not quantified) and N$_2$O; the concentrations of NO and NO$_2$ in the product gas were below detection limit. Nitrous oxide is formed in significant amounts, reaching 50 ppm in the alumina reactor and levels above 100 ppm in the quartz reactor at 900 K.

At 100 bar (Fig. 7), reaction is initiated already at 800-825 K, partly due to the longer residence time, and NH$_3$ is fully oxidized at 875-900 K. The N$_2$O concentration approaches 200 ppm, corresponding to a selectivity for forming N$_2$O from NH$_3$ of about 50%. The N$_2$O profiles from the quartz and alumina reactors indicate a difference in onset temperature, but the peak concentrations are similar.

The model predicts satisfactorily the experimental data. The best agreement is obtained for the alumina reactor data, which are possibly more reliable. At 30 bar, the agreement is very good, while at 100 bar the temperature for onset of reaction is slightly overpredicted. The most important difference is that the concentration of N$_2$O is underpredicted at the highest pressure. In line with observations, the model predicts that any NO or NO$_2$ formed are rapidly consumed.

Figure 8 shows the results of a rate of production analysis under oxidizing conditions. The arrow thickness distinguishes the main and minor routes for ammonia consumption. Results are shown for 100 bar conditions, but the reaction paths are similar for 30 bar. The main oxidation for ammonia is NH$_3$ + OH $\rightarrow$ NH$_2$ + HO$_2$ NO $\rightarrow$ H$_2$NO $\rightarrow$ HNO $\rightarrow$ NO $\rightarrow$ NO $\rightarrow$ NH$_2$ $\rightarrow$ N$_2$. Ammonia is mainly consumed through the reaction NH$_3$ + OH = NH$_2$ + H$_2$O (R4). The peroxide radical HO$_2$ is the main chain carrier under the present conditions.
with high pressure and low to intermediate temperatures. However, HO₂ is partly converted to OH through the fast steps,

\[ \text{NO} + \text{HO}_2 \rightleftharpoons \text{NO}_2 + \text{OH} \]

\[ \text{NH}_2 + \text{HO}_2 \rightleftharpoons \text{H}_2\text{NO} + \text{OH} \]  \hspace{1cm} \text{(R11)}

In addition to (R11), the NH₂ radical reacts mainly with NO₂,

\[ \text{NH}_2 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O} + \text{H}_2\text{O} \]  \hspace{1cm} \text{(R20)}

\[ \text{NH}_2 + \text{NO}_2 \rightleftharpoons \text{H}_2\text{NO} + \text{NO} \]  \hspace{1cm} \text{(R21)}

Most of the NH₂ is converted to H₂NO (R11, R21). Nitrooxide then reacts with O₂ (R29), HO₂ (R28), and NO₂ (R31); these steps all abstract a hydrogen atom from H₂NO to form HNO, which is converted to NO by reaction with O₂ (R32).

\[ \text{H}_2\text{NO} + \text{O}_2 \rightleftharpoons \text{HNO} + \text{HO}_2 \]  \hspace{1cm} \text{(R29)}

\[ \text{H}_2\text{NO} + \text{HO}_2 \rightleftharpoons \text{HNO} + \text{H}_2\text{O}_2 \]  \hspace{1cm} \text{(R28)}

\[ \text{H}_2\text{NO} + \text{NO}_2 \rightleftharpoons \text{HNO} + \text{HONO} \]  \hspace{1cm} \text{(R31)}

\[ \text{HNO} + \text{O}_2 \rightleftharpoons \text{NO} + \text{HO}_2 \]  \hspace{1cm} \text{(R32)}

Finally, NO reacts with HO₂ or NH₂. The NH₂ + NO reaction leads to formation of N₂, either directly

\[ \text{NH}_2 + \text{NO} \rightleftharpoons \text{N}_2 + \text{H}_2\text{O} \]  \hspace{1cm} \text{(R18)}

or via

\[ \text{NH}_2 + \text{NO} \rightleftharpoons \text{NNH} + \text{OH} \]  \hspace{1cm} \text{(R19)}

followed by rapid dissociation of NNH (R33) or reaction with O₂ (R34).
The reaction $\text{NH}_2 + \text{NO}_2 = \text{N}_2\text{O} + \text{H}_2\text{O}$ (R20) is the main source of $\text{N}_2\text{O}$ at both 30 bar and 100 bar oxidizing conditions. A minor route for consumption of $\text{NH}_2$ is the recombination reaction to form hydrazine,

$$\text{NH}_2 + \text{NH}_2(+\text{M}) \rightleftharpoons \text{N}_2\text{H}_4(+\text{M})$$

Figure 9 shows the results of a sensitivity analysis for oxidizing conditions at 30 and 100 bar. The coefficients were obtained by varying A-factors for all reactions by a factor of two. Reactions of $\text{NH}_2$ with $\text{NO}$ and $\text{NO}_2$ are important for the oxidation rate. For both reactions a chain propagating / branching product channel,

$$\text{NH}_2 + \text{NO} \rightleftharpoons \text{NNH} + \text{OH} \quad \text{(R19)}$$
$$\text{NH}_2 + \text{NO}_2 \rightleftharpoons \text{H}_2\text{NO} + \text{NO} \quad \text{(R21)}$$
competes with a chain terminating channel,

$$\text{NH}_2 + \text{NO} \rightleftharpoons \text{N}_2 + \text{H}_2\text{O} \quad \text{(R18)}$$
$$\text{NH}_2 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O} + \text{H}_2\text{O} \quad \text{(R20)}$$

All these steps show up in the sensitivity analysis with large positive (branching) or negative (terminating) coefficients.

Other important reactions which accelerate ammonia consumption are,

$$\text{NH}_2 + \text{HO}_2 \rightleftharpoons \text{H}_2\text{NO} + \text{OH} \quad \text{(R11)}$$
$$\text{H}_2\text{NO} + \text{O}_2 \rightleftharpoons \text{HNO} + \text{HO}_2 \quad \text{(R29)}$$

The reaction $\text{H}_2\text{NO} + \text{O}_2$ (R29) has the largest positive sensitivity coefficients. $\text{H}_2\text{NO}$ is a significant intermediate species as shown in the reaction path analysis and (R29) is favored by the excess of $\text{O}_2$ in oxidizing conditions.
It yields HO$_2$ radicals, which is converted to the more reactive OH radical by NH$_2$ + HO$_2$ (R11).

The following chain terminating steps inhibit the ammonia consumption,

\[
\begin{align*}
H_2\text{NO} + \text{HO}_2 &\rightleftharpoons \text{HNO} + \text{H}_2\text{O}_2 & \text{(R28)} \\
H_2\text{NO} + \text{NO}_2 &\rightleftharpoons \text{HONO} + \text{HNO} & \text{(R31)} \\
\text{NH}_2 + \text{NH}_2(\text{+M}) &\rightleftharpoons \text{N}_2\text{H}_4(\text{+M})
\end{align*}
\]

Reactions (R28) and (R31) are minor consumption channels for H$_2$NO, compared to H$_2$NO + O$_2$ (R29), but sufficiently important to show up in the sensitivity analysis. Similarly, NH$_2$ + NH$_2$(+M) is a minor sink for NH$_2$, but it is strongly chain terminating.

The results show that to develop a reliable reaction mechanism for NH$_3$ oxidation at the present conditions, it is desirable to obtain more accurate rate constants for several reactions in the H$_2$NO subset.

**Conclusions**

Ammonia oxidation experiments were conducted at high pressure (30 bar and 100 bar) and temperatures of 450-900 K in oxidizing and stoichiometric conditions. The data were interpreted in terms of a detailed chemical kinetic model, developed for high-pressure conditions. As part of the work, the rate constant for the reaction of H$_2$NO + O$_2$ was calculated from ab initio theory.

The oxidation of ammonia was slow under stoichiometric conditions in the temperature range investigated. Under oxidizing conditions the onset temperature for reaction was 850-875 K at 30 bar, while at 100 bar it was about
800 K, with complete consumption of NH₃ at 875 K. The products of reaction were N₂ and N₂O, while NO and NO₂ concentrations were below the detection limit even under oxidizing conditions.

The agreement between experimental results and modelling work was satisfactory. The main oxidation path for NH₃ under the present conditions was

\[
\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{HO}_2 \rightarrow \text{NO} \rightarrow \text{NO} \rightarrow \text{HNO} \rightarrow \text{NO} \rightarrow \text{NH}_2 \rightarrow \text{N}_2.
\]

The modeling predictions were most sensitive to the reactions NH₂ + NO = NNH + OH and NH₂ + HO₂ = H₂NO + OH, which promoted the ammonia consumption by forming OH radicals, and to NH₂ + NO = N₂ + H₂O and NH₂ + NO₂ = N₂O + H₂O, which were the main chain-terminating steps.

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**References**


[43] Altinay G, Macdonald RG. Determination of the Rate Constants for the NH₂(X²B₁) + NH₂(X²B₁) and NH₂(X²B₁) + H Recombination Reactions in N₂ as a Function of Temperature and Pressure, J Phys Chem A 2015;119:7593-7610.


[50] Mebel AM, Dian EWG, Lin MC, Morokuma K. Theoretical Rate Constants for the \( \text{NH}_3 + \text{NO}_x \rightarrow \text{NH}_2 + \text{HNO}_x \) \((x=1,2)\) Reactions by Ab Initio MO/VTST Calculations. J Phys Chem 1996;100:7517-7525.


[52] Sun F, DeSain JD, Scott G, Hung PY, Thompson RI, Glass GP, Curl RF. Reactions of \( \text{NH}_2 \) with \( \text{NO}_2 \) and of \( \text{OH} \) with \( \text{NH}_2\text{O} \). J Phys Chem A 2001;105:6121-6128.


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<td>10.</td>
<td>NH₂ + OH ⇌ NH + H₂O</td>
<td>3.3E06</td>
<td>1.949</td>
<td>-217</td>
</tr>
<tr>
<td>11.</td>
<td>NH₂ + HO₂ ⇌ H₂NO + OH</td>
<td>5.0E13</td>
<td>0.000</td>
<td>0</td>
</tr>
<tr>
<td>12.</td>
<td>NH₂ + HO₂ ⇌ HNO + H₂O</td>
<td>1.6E07</td>
<td>0.550</td>
<td>525</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>5.7E15</td>
</tr>
<tr>
<td>13.</td>
<td>NH₂ + HO₂ ⇌ HONO + H₂O</td>
<td>2.1E07</td>
<td>0.640</td>
<td>811</td>
</tr>
<tr>
<td>14.</td>
<td>NH₂ + O₂ ⇌ H₂NO + O</td>
<td>2.6E11</td>
<td>0.487</td>
<td>29050</td>
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<tr>
<td>15.</td>
<td>NH₂ + O₂ ⇌ HONO + OH</td>
<td>2.9E-2</td>
<td>3.764</td>
<td>18185</td>
</tr>
<tr>
<td>16.</td>
<td>NH₂ + NH₂ ⇌ NH₃ + NH</td>
<td>5.6E00</td>
<td>3.530</td>
<td>552</td>
</tr>
<tr>
<td>17.</td>
<td>NH₂ + HNO ⇌ NH₃ + NO</td>
<td>3.6E06</td>
<td>1.630</td>
<td>-1250</td>
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<tr>
<td>18.</td>
<td>NH₂ + NO ⇌ N₂ + H₂O</td>
<td>1.3E16</td>
<td>-1.25</td>
<td>0</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-3.1E13</td>
</tr>
<tr>
<td>19.</td>
<td>NH₂ + NO ⇌ NNH + OH</td>
<td>3.1E13</td>
<td>-0.48</td>
<td>1180</td>
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<td>20.</td>
<td>NH₂ + NO₂ ⇌ N₂O + H₂O</td>
<td>2.6E18</td>
<td>-2.191</td>
<td>455</td>
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<tr>
<td>21.</td>
<td>NH₂ + NO₃ ⇌ H₂NO + NO</td>
<td>9.1E11</td>
<td>0.032</td>
<td>-1512</td>
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<tr>
<td>22.</td>
<td>NH₂ + HONO ⇌ NH₃ + NO₂</td>
<td>7.1E01</td>
<td>3.020</td>
<td>-4940</td>
</tr>
<tr>
<td>23.</td>
<td>H₂NO + M ⇌ HNO + H + M</td>
<td>2.8E24</td>
<td>-2.830</td>
<td>64915</td>
</tr>
<tr>
<td>24.</td>
<td>H₂NO + H ⇌ HNO + H₂</td>
<td>3.0E07</td>
<td>2.000</td>
<td>2000</td>
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<tr>
<td>25.</td>
<td>H₂NO + H ⇌ NH₂ + OH</td>
<td>5.0E13</td>
<td>0.000</td>
<td>0</td>
</tr>
<tr>
<td>26.</td>
<td>H₂NO + O ⇌ HNO + OH</td>
<td>3.0E07</td>
<td>2.000</td>
<td>2000</td>
</tr>
<tr>
<td>27.</td>
<td>H₂NO + OH ⇌ HNO + H₂O</td>
<td>1.6E14</td>
<td>0.000</td>
<td>0</td>
</tr>
<tr>
<td>28.</td>
<td>H₂NO + HO₂ ⇌ HNO + H₂O₂</td>
<td>2.9E04</td>
<td>2.600</td>
<td>-1600</td>
</tr>
<tr>
<td>29.</td>
<td>H₂NO + O₂ ⇌ HNO + HO₂</td>
<td>2.3E02</td>
<td>2.994</td>
<td>18900</td>
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<tr>
<td>30.</td>
<td>H₂NO + NH₂ ⇌ HNO + NH₃</td>
<td>3.0E12</td>
<td>0.000</td>
<td>1000</td>
</tr>
<tr>
<td>31.</td>
<td>H₂NO + NO₂ ⇌ HONO + HNO</td>
<td>6.0E11</td>
<td>0.000</td>
<td>2000</td>
</tr>
<tr>
<td>Reaction</td>
<td>Products</td>
<td>A</td>
<td>E (E)</td>
<td>K (cm^3 mol^-1 s^-1)</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>---</td>
<td>-------</td>
<td>---------------------</td>
</tr>
<tr>
<td>HNO + O₂ → NO + HO₂</td>
<td>2.0E13</td>
<td>0.000</td>
<td>16000</td>
<td>[33]</td>
</tr>
<tr>
<td>NNH = N₂ + H</td>
<td>1.0E09</td>
<td>0.000</td>
<td>0</td>
<td>[38]</td>
</tr>
<tr>
<td>NNH + O₂ → N₂ + HO₂</td>
<td>5.6E14</td>
<td>-0.385</td>
<td>-13</td>
<td>[38]</td>
</tr>
</tbody>
</table>

a: Rate constant calculated for 1 atm.
b: Duplicate reaction – the resulting rate constant is the sum of the two expressions.

Table 1: Selected reactions from the NH₃ subset. Parameters for use in the modified Arrhenius expression k = AT^β exp(-E/[RT]). Units are mol, cm, s, cal.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Inlet composition&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Pressure</th>
<th>Temperature</th>
<th>Residence time&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>772 ppm NH&lt;sub&gt;3&lt;/sub&gt;, 929 ppm O&lt;sub&gt;2&lt;/sub&gt; (ϕ = 1.04)</td>
<td>30</td>
<td>4504925</td>
<td>3100/T[K]</td>
<td>Quartz</td>
</tr>
<tr>
<td>2</td>
<td>714 ppm NH&lt;sub&gt;3&lt;/sub&gt;, 861 ppm O&lt;sub&gt;2&lt;/sub&gt; (ϕ = 1.03)</td>
<td>100</td>
<td>4504925</td>
<td>10330/T[K]</td>
<td>Quartz</td>
</tr>
<tr>
<td>3</td>
<td>729 ppm NH&lt;sub&gt;3&lt;/sub&gt;, 3.95% (v) O&lt;sub&gt;2&lt;/sub&gt; (ϕ = 0.23)</td>
<td>30</td>
<td>4504925</td>
<td>3100/T[K]</td>
<td>Quartz</td>
</tr>
<tr>
<td>4</td>
<td>719 ppm NH&lt;sub&gt;3&lt;/sub&gt;, 4.03% (v) O&lt;sub&gt;2&lt;/sub&gt; (ϕ = 0.22)</td>
<td>30</td>
<td>4504925</td>
<td>1984/T[K]</td>
<td>Alumina</td>
</tr>
<tr>
<td>5</td>
<td>789 ppm NH&lt;sub&gt;3&lt;/sub&gt;, 4.07% (v) O&lt;sub&gt;2&lt;/sub&gt; (ϕ = 0.24)</td>
<td>100</td>
<td>4504925</td>
<td>10330/T[K]</td>
<td>Quartz</td>
</tr>
<tr>
<td>6</td>
<td>789 ppm NH&lt;sub&gt;3&lt;/sub&gt;, 4.07% (v) O&lt;sub&gt;2&lt;/sub&gt; (ϕ = 0.24)</td>
<td>100</td>
<td>4504925</td>
<td>6610/T[K]</td>
<td>Alumina</td>
</tr>
</tbody>
</table>

<sup>a</sup> Volume basis; balance N<sub>2</sub>

<sup>b</sup> The nominal residence time in the isothermal region of the reactor. It is a function of temperature, since the mass flow rate was held constant.

Table 2: Experimental conditions for the NH<sub>3</sub> oxidation study.
Figure 1: Measured temperature profiles along the reactor axis for 100 bar conditions.
Figure 2: UQCISD/6-311G(d,p) geometries of $^2A'$ H$_2$NO, the planar $^2B_1$ barrier to inversion, and the transition state for abstraction of H by O$_2$. Distances are in Å and angles in degrees. Dihedral angles in the TS: HNHO -159.2°, OHNH -49.2°, OOHN -24.2°.
Figure 3: The double-well potential of H$_2$NO computed at the UQCISD/6-311G(d,p) level of theory. The barrier height and the first three eigenvalues for out-of-plane bending are relative to the minima. The angle is defined as the deviation from 180° (the planar conformation) for the angle O-N-X where X is a point midway between the two H atoms.
Figure 4: Comparison of experimental and predicted concentration profiles as a function of the reactor temperature for the stoichiometric experiment at 30 bar in the quartz reactor. The symbols mark experimental data while solid lines denote model predictions obtained at isothermal conditions. Inlet composition: 772 ppm NH₃, 929 ppm O₂; balance N₂. The fuel-air equivalence ratio is $\phi = 1.04$ and the residence time in the isothermal zone is calculated from $\tau[s] = 3100/T[K]$. 
Figure 5: Comparison of experimental and predicted concentration profiles as a function of the reactor temperature for the stoichiometric experiment at 100 bar in the quartz reactor. The symbols mark experimental data while solid lines denote model predictions obtained at isothermal conditions. Inlet composition: 714 ppm NH$_3$, 864 ppm O$_2$; balance N$_2$. The fuel-air equivalence ratio is $\phi = 1.03$ and the residence time in the isothermal zone is calculated from $\tau [s] = 10330 / T [K]$. 
Figure 6: Comparison of experimental and predicted concentration profiles as a function of the reactor temperature for the oxidizing experiment at 30 bar, obtained in a quartz and alumina tube, respectively. The symbols mark experimental data while solid lines denote model predictions obtained at isothermal conditions. Inlet composition: 729 ppm NH₃, 3.95%(v) O₂; balance N₂. The fuel-air equivalence ratio is $\phi = 0.23$ and the residence time in the isothermal zone is calculated from $\tau_s = 3100/K$ for the quartz tube and $\tau_s = 1984/K$ for the alumina tube.
Figure 7: Comparison of experimental and predicted concentration profiles as a function of the reactor temperature for the oxidizing experiment at 100 bar, obtained in a quartz and alumina tube, respectively. The symbols mark experimental data while solid lines denote model predictions obtained at isothermal conditions. Inlet composition: 789 ppm NH₃, 4.07% (v) O₂; balance N₂. The fuel-air equivalence ratio is φ = 0.24 and the residence time in the isothermal zone is calculated from τ[s] = 10330 / T[K] for the quartz tube and τ[s] = 6610 / T[K] for the alumina tube.
Figure 8: Main reaction pathways for NH$_3$ oxidation at the investigated conditions. The diagram is based on the 100 bar oxidizing condition at a temperature of 875 K, but reaction paths are similar at 30 bar oxidizing conditions.
Figure 9: First order sensitivity coefficients for NH₃ for conditions of 30 bar (925 K) and 100 bar (900 K).