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# An experimental, theoretical and kinetic-modeling study of the gas-phase oxidation of ammonia

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## Abstract

A complete understanding of the mechanism of ammonia pyrolysis and oxidation in the full range of operating conditions displayed by industrial applications is one of the challenges of modern combustion kinetics. In this work, a wide-range investigation of the oxidation mechanism of ammonia was performed. Experimental campaigns were carried out in a jet-stirred reactor and a flow reactor under lean conditions ( $0.01 \leq \Phi \leq 0.375$ ), such to cover the full range of operating temperatures ( $500 \text{ K} \leq T \leq 2000 \text{ K}$ ). Ammonia conversion and the formation of products and intermediates were analyzed. At the same time, the ammonia decomposition reaction, H-abstractions and the decomposition of the HNO intermediate were evaluated ab initio, and the related rates were included in a comprehensive kinetic model, developed according to a first-principles approach. Low-temperature reactor experiments highlighted a delayed reactivity of ammonia, in spite of the high amount of oxygen. A very slow increase in  $\text{NH}_3$  consumption rate with temperature was observed, and a full reactant consumption was possible only  $\sim 150\text{--}200 \text{ K}$  after the reactivity onset. The use of flux analysis and sensitivity analysis allowed explaining this effect with the terminating effect of the H-abstraction on  $\text{NH}_3$  by  $\text{O}_2$ , acting in the reverse direction because of the high amounts of  $\text{HO}_2$ . The central role of  $\text{H}_2\text{NO}$  was observed at low temperatures ( $T < 1200 \text{ K}$ ), and H-abstractions from it by  $\text{HO}_2$ ,  $\text{NO}_2$  and  $\text{NH}_2$  were found to control reactivity, especially at higher pressures. On the other side, the formation of HNO intermediate via  $\text{NH}_2 + \text{O} = \text{HNO} + \text{H}$  and its decomposition were found to be crucial at higher temperatures, affecting both  $\text{NO}/\text{N}_2$  ratio and flame propagation.

**Keywords:** ammonia, jet-stirred reactor, flow reactor, detailed kinetics, ab initio

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## 1. Introduction

The gradual transition towards newer and more sustainable energy sources for combustion applications is being carried out by pursuing two major targets: (i) a smarter, more efficient use of the available resources, in such a way to reduce energy wastes and CO<sub>2</sub> emissions, and (ii) a systematic control of pollutant emissions, which are formed as byproducts of the combustion processes. In this context, the scientific interest towards ammonia (NH<sub>3</sub>) has been significantly increasing in the last years. As a matter of fact, the high energy density, ease of transportation and carbon-free nature of ammonia make it an attractive candidate as an energy vector: considering that its production relies on established production technologies as well as on a number of novel synthesis techniques,<sup>1,2</sup> NH<sub>3</sub> has also been proposed as a “platform molecule” for the energy storage from intermittent renewable sources (i.e. wind or sun), and based on successive release via either direct combustion or earlier conversion to hydrogen.<sup>3</sup> The competitiveness of ammonia as an energy carrier for the accumulation of excess energy and its release “on-demand” has been assessed in several works.<sup>4,5</sup> Moreover, its relevance in the next-generation energy scenario is also connected to its presence (in trace amounts) in biofuels: indeed, ammonia is found in biogas as a by-product of anaerobic digestion.<sup>6,7</sup> In addition, protein-rich sludges used as raw materials for bio-oils also contain NH<sub>3</sub> as well as other nitrogenated species.<sup>8</sup>

The research on the ammonia combustion chemistry actually started several decades ago. The high-temperature pyrolysis mechanism was first experimentally characterized starting from the 1980s,<sup>9-12</sup> with modelling work carried out in parallel.<sup>12,13</sup> Studies on oxidation focused first on NH<sub>3</sub> flame chemistry<sup>14-16</sup> and on its use within the Thermal DeNO<sub>x</sub> process<sup>17</sup> for the selective non-catalytic reduction of nitrogen oxides (NO<sub>x</sub>). Later, oxidation chemistry was studied at a fundamental level through targeted experiments<sup>18-20</sup> and theoretical methodologies.<sup>21-24</sup> As a result, NH<sub>3</sub> kinetic mechanisms have largely benefited from incremental improvements. One of the first mechanisms was released by Miller et al.,<sup>15</sup> who later included NH<sub>3</sub> chemistry in their review work on nitrogen compounds.<sup>25</sup> Since then, many dedicated models describing ammonia combustion were released. Konnov and De Ruyck<sup>26</sup> extended the pyrolysis mechanism initially developed by Davidson et al.<sup>12</sup> by including the reactions of N<sub>2</sub>H<sub>3</sub> and N<sub>2</sub>H<sub>4</sub>, which were shown to have an important effect on NH and NH<sub>2</sub> profiles. Mathieu and Petersen<sup>27</sup> extended the work of Dagaut et al.<sup>28</sup> on HCN chemistry to model the high-temperature ignition delay times of NH<sub>3</sub>, collected under diluted conditions at different pressures and equivalence ratios. Shrestha et al.<sup>29</sup> recently presented a mechanism for the oxidation of NH<sub>3</sub> and NH<sub>3</sub>/H<sub>2</sub> fuel blends, validated in several 0D and 1D systems, while Li et al.<sup>30</sup> developed two reduced mechanisms for the combustion of NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/H<sub>2</sub>/CH<sub>4</sub> mixtures in air. The review work by Glarborg et al.<sup>31</sup> also includes ammonia pyrolysis and oxidation mechanism in their comprehensive nitrogen kinetic model, and provides an exhaustive overview of the state of the art in the kinetic modelling of NH<sub>3</sub> oxidation.

On the other hand, several experimental campaigns carried out in the latest years in less conventional conditions (lower temperatures, high dilution levels and wider pressure ranges) have shown that the fundamental knowledge of ammonia kinetics is still far from complete: the available mechanisms

have shown important deviations in the autoignition behavior in diluted conditions, both in high-temperature shock tubes (ST)<sup>27</sup> and low- to intermediate-temperature shock tubes<sup>32</sup> and rapid compression machines (RCM).<sup>33,34</sup> Similarly, flow reactor experiments of pure NH<sub>3</sub> oxidation under atmospheric<sup>35</sup> and high pressure<sup>36</sup> showed that the kinetic models were not always able to reproduce the experimental trends. Da Rocha et al.<sup>37</sup> showed the inadequacy of several kinetic mechanisms in predicting the laminar flame speed (LFS) of NH<sub>3</sub>, and most of them were shown to overpredict the actual rates.

In order to ensure an adequate degree of comprehensiveness, a fundamental understanding of ammonia kinetics still needs to be achieved. Glarborg et al.<sup>31</sup> pointed out the most unclear pathways of the NH<sub>3</sub> oxidation mechanism: they showed that the largest uncertainties are present under low-temperature conditions, especially with high concentrations of oxygen. In such cases, the role of intermediates, such as H<sub>2</sub>NO and HNO, was shown to be determining, as well as the interaction of the HO<sub>2</sub> radical with the radical pool (e.g. NH<sub>2</sub> and NO). At the same time, the experimental data under these operating conditions in support of a proper model development are still very limited.

Starting from this scenario, the aim of this work is filling the void of knowledge still remaining in the kinetic mechanisms involved in the oxidation of ammonia, with a focus on the critical conditions previously mentioned, and scarcely explored so far. To this purpose, new experimental measurements were performed in a jet-stirred reactor (JSR) and a flow reactor (FR), such as to explore the low- and intermediate-temperature oxidation of ammonia with high dilution levels. At the same time, the critical rate constants involved in the ammonia combustion mechanism were systematically evaluated through a first-principles methodology. In particular, NH<sub>3</sub> decomposition, as well as H-abstractions by O<sub>2</sub>, H, O, OH and HO<sub>2</sub>, and the dissociation of the HNO intermediate are discussed. The calculated values were then exploited for a wide-range kinetic modeling of ammonia pyrolysis and oxidation, including the state-of-the-art kinetic constants made available in the latest years. This is used to interpret and explain the experimental results obtained in the two reactors. Finally, the comprehensive capability of the kinetic mechanism in predicting ammonia combustion in different configurations (ST, RCM, FR, LFS and Burner-Stabilized Flame - BSF) and operating conditions was assessed, highlighting the most critical competitive paths, still needing attention at a theoretical level.

## **2. Methodology**

### **2.1. Experimental setup**

The experimental measurements were performed using two different reactors, a jet-stirred reactor (JSR) and a tubular flow reactor (FR) working close to atmospheric pressure, in order to explore the low, intermediate and high temperature oxidation of ammonia with high dilution levels by using helium as carrier gas. Bronkhorst mass flow controllers are used for reactor feeding (relative uncertainty of ±0.5% in flow). Helium (99.999% pure) and O<sub>2</sub> (99.999%) were provided by Messer.

A cylinder of  $2004 \pm 60$  ppm ammonia diluted in helium, also provided by Messer, was used for the feed of ammonia.

In a first set-up, experiments were carried out in a fused silica JSR, a type of continuous stirred-tank reactor usually operated at steady state. JSRs were often used in gas phase kinetic studies. The present JSR setup was already described in previous works.<sup>38-40</sup> Briefly, it consisted of a spherical vessel with an injection of the preheated fresh mixture through four nozzles located at the center of the reactor, which produce high turbulence leading to homogeneity in temperature and composition. The preheating and heating of the reactor were performed using Inconel Thermocoax resistances rolled around the different parts and controlled by independent K-type thermocouples. A K-type thermocouple located in a glass finger close to the center of the reactor was used to measure the reaction temperature (uncertainty of  $\pm 5$  K), which is considered as isothermal when running simulations. Pressure was set to 800 torr (106.7 kPa).

A second setup (Figure 1) was specifically developed to explore  $\text{NH}_3$  oxidation at higher temperature (up to  $\sim 2000$  K) in a flow reactor (FR). It consisted of a tube made of recrystallized alumina (inner diameter of 4 mm and 100 cm in length), designed to approximate a plug flow reactor. Its operating pressure was 950 torr (126.7 kPa). Under the studied conditions, the Reynolds number was found to vary between 146 and 75, thus the flow was laminar. The Peclet number,  $Pe = u \times d/D$  ( $u$  is the linear velocity of the gas,  $d$  is the internal diameter of the tube, and  $D$  is the molecular diffusivity of helium) was calculated as a function of temperature. The calculation provides values ranging from  $\sim 900$  at  $\sim 1100$  K to  $\sim 450$  at  $\sim 2000$  K, supporting the hypothesis that diffusion has a minor impact on the flow ( $Pe > 100$ ) and that the reactor can be modelled as a plug flow reactor.<sup>41</sup>

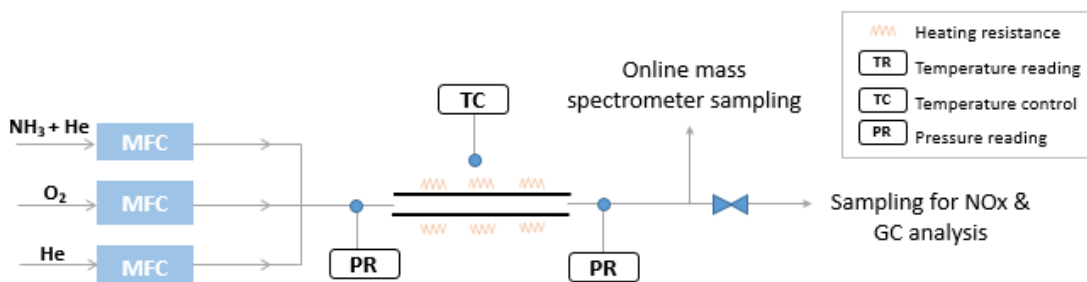


Figure 1 - Scheme of the experimental facility (flow reactor).

The reactor was located horizontally in an electrically-heated oven (Carbolite Gero) which has an internal regulation. Actual temperature profiles were measured by an R-type thermocouple under unreactive conditions for each set-point temperature. Temperatures were recorded with a step of 2 cm in the isothermal region, and every 5 cm on both sides of the isothermal region. This isothermal reaction zone is located between 36 and 58 cm as shown in Figure 2, with a quasi-uniform temperature profile ( $\pm 30$  K). The residence time is about 50 ms in the central zone where the temperature can be considered as constant. Flow rates were varied for each temperature set-point to

maintain the residence time constants. Both temperature profiles and flow rate calculations are available as Supplementary Material.

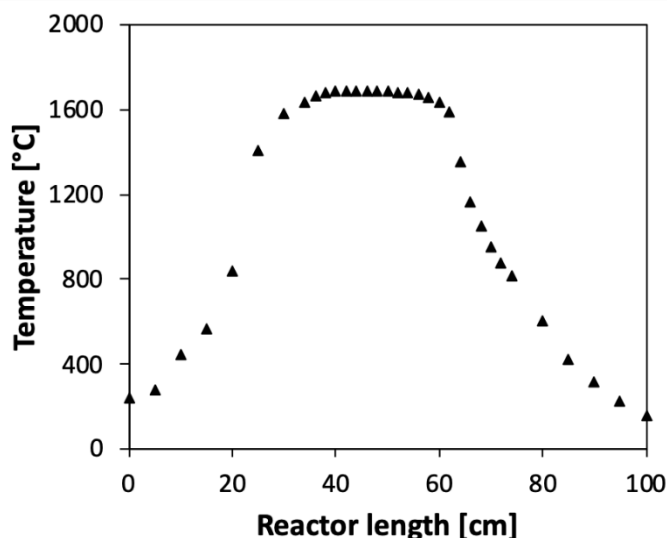


Figure 2 - Temperature profile measured (set point of 1700°C) in the tubular flow reactor in absence of reaction.

It is important to point out that significant catalytic effects of the reactor wall were first suspected in FR in the absence of oxygen when using non-recrystallized alumina. To confirm this, the following protocol was followed:

1. Ammonia pyrolysis was first performed in a non-recrystallized alumina tube, in order to have a reference for comparison.
2. Then, the tube wall was coated with carbonaceous material by carrying out methane pyrolysis in the non-recrystallized alumina tube.
3. After coating, ammonia pyrolysis was repeated, and a significant shift of the reactivity of  $\sim 500$  K towards lower temperatures was observed.

As a result, the tube was replaced and recrystallized alumina was adopted (with a higher purity than alumina). This resulted in a global shift of the reactivity of  $\sim 100$  K towards higher temperatures when compared to the data obtained with the non-coated, non-recrystallized alumina first tube, and provided data consistent with model predictions.

Another evidence for the occurrence of wall interactions was the long time needed to reach steady state when flowing the reacting mixture (several tens of minutes). This was observed thanks to the use of online mass spectrometry with direct sampling in the gas phase at the outlet of the tube. Such stabilization time was considerably shortened when using a recrystallized alumina tube (a few minutes).

The reactants and reaction products were identified and quantified by using four complementary analytical techniques:

i. **Online gas chromatography** was used for the quantification of H<sub>2</sub> during the NH<sub>3</sub> oxidation in FR. It was equipped with a Carbosphere packed column (the carrier gas was argon), and a thermal conductivity detector (TCD). Argon was used as carrier gas to detect H<sub>2</sub> with a good sensitivity. The sampling was achieved in the outlet flow of the reactor using a sampling loop mounted on a six-way valve. Calibrations were performed using gaseous standards. The relative uncertainty in H<sub>2</sub> mole fraction is  $\pm 5\%$ .

ii. **On-line mass spectrometry** (Omnistar from Pfeiffer) with ionization at 70 eV was used to detect NH<sub>3</sub>, N<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub> in FR experiments. Sampling was carried out through a capillary tube directly connecting the reactor outlet and the analyzer under vacuum and sucking a constant flow. This technique requires the calibration of each species as there is no obvious relationship between their molecule structures and their calibration factors. Gaseous standards were used except for water, which was calibrated considering the reaction complete at the highest temperature. Note that this technique offers the possibility to follow the evolution of the different masses of interest as a function of the time and to check for steady state conditions to be reached. The relative uncertainty in NH<sub>3</sub>, N<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub> mole fractions was estimated to be  $\pm 10\%$ .

iii. **A continuous-wave cavity ring-down spectroscopy** (cw-CRDS) cell coupled to the JSR by a sonic probe was used for NH<sub>3</sub> quantification. This technique is based on the absorption of species in the infrared, as for the FTIR technique. It is much more sensitive as the light path is much longer. It was already used in previous studies to quantify intermediates like hydrogen peroxide and HONO during the oxidation of fuels.<sup>42,43</sup> Ammonia has strong absorption lines in the wavenumber range 6637–6643 cm<sup>-1</sup>, making the quantification accurate and providing a good sensibility. Figure 3 displays an extract of a spectrum recorded during the present study under unreactive condition ( $\Phi = 1$ ,  $T = 500$  K). The whole spectrum recorded over the range 6637–6643 cm<sup>-1</sup> is given in the Supplementary Material. Two intense lines were used to quantify ammonia with a good sensitivity: 6641.33 and 6642.57 cm<sup>-1</sup>. Cross sections needed for the calibrations were measured using data recorded under unreactive conditions. The relative uncertainty in NH<sub>3</sub> mole fraction detected by CRDS is  $\pm 10\%$ .

iv. A dual channel NO<sub>x</sub> chemiluminescence analyzer (Thermo Scientific Model 42i) was used for the detection of NO and NO<sub>2</sub> (but no NO<sub>2</sub> was detected in these experiments). The detection is based on the conversion of NO (with ozone) to an excited state of NO<sub>2</sub> that emits a chemiluminescent light when dropping to the ground state. On the first channel, the detection of nitric oxide is performed in a direct and independent way, whereas the second channel is dedicated to the measure of the total NO<sub>x</sub> concentration. In this second channel, the sampled gas passes over a heated catalyst transforming nitrogen oxides to nitric oxide, NO, which is detected by chemiluminescence as in the first channel. NO<sub>2</sub> concentration is then deduced by subtracting the concentration of NO from that of the total NO<sub>x</sub>. Note that this analyzer is equipped by an ammonia trap to avoid the interference of this species.

Calibrations were performed using gaseous standards. The relative uncertainty in NO mole fraction is  $\pm 5\%$ , while that of NO<sub>2</sub> mole fraction is 10% since it is measured by difference.

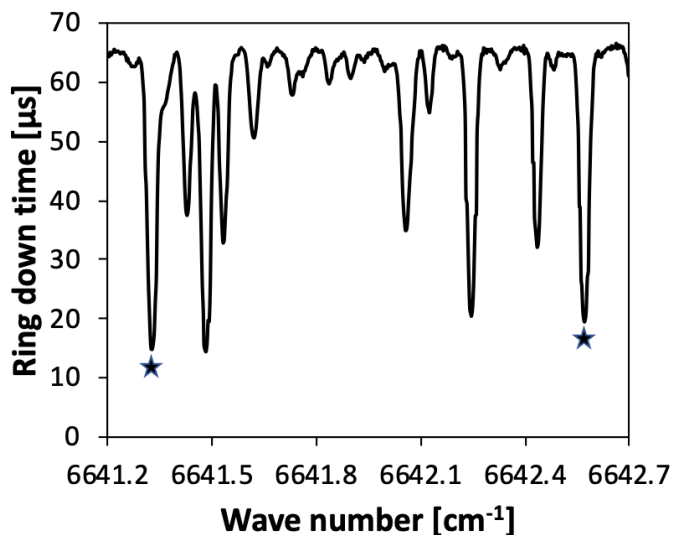


Figure 3 - Extract of the CRDS infrared spectrum recorded during the oxidation of ammonia under unreactive conditions ( $\Phi = 1$ ,  $T = 500$  K). The two star symbols indicate the two intense lines which were used for the quantification of ammonia.

## 2.2 Theoretical methodologies

The rate constants of a specific set of reactions were determined theoretically. They were identified on the basis of a combined uncertainty and sensitivity analysis with respect to the explored experimental conditions as well as on the availability of previous experimental/theoretical studies for each of them. The adopted computational methodology is the ab initio transition state theory based master equation (ME) approach (AITSTME) that was recently implemented in the EStokTP software.<sup>44</sup> Electronic structure calculations for abstraction reactions were performed determining structures and vibrational frequencies at the M06-2X/aug-cc-pVTZ level and energies at the unrestricted CCSD(T)/aug-cc-pVTZ level, corrected for basis set size effect with the change of density fitted (DF) MP2 energies computed using aug-cc-pVQZ and aug-cc-pVTZ basis sets. Rate constants were estimated using variational transition state theory (VTST), as implemented in MESS<sup>45</sup> for both reactions exhibiting a saddle point on the minimum energy path (MEP) and for barrierless reactions. For abstraction reactions, the structure and energies of van der Waals wells on entrance and exit channels were determined at the M06-2X/aug-cc-pVTZ level of theory. For H-abstraction from NH<sub>3</sub> by OH, whose CCSD(T) wavefunction has a large T1 diagnostic of 0.056, the energy barrier was computed performing multireference calculations at the CASPT2/aug-cc-pVTZ level using a full valence (15e,12o) active space. Hindered rotors were treated in the 1D hindered rotor approximation with torsional potential energy surfaces (PES) determined at the M06-2X/6-311+G(d,p) level. Torsional motions were projected out of the Hessian when calculating harmonic frequencies.<sup>44</sup>



Harmonic frequencies and MEP energies for barrierless reactions (NH<sub>3</sub> and HNO decomposition) were determined at the CASPT2/aug-cc-pVTZ level using a full valence active space. In the case of HNO decomposition, the wavefunction was state averaged over two states. All density functional theory (DFT) calculations were performed using the G09 computational suite,<sup>46</sup> while CCSD(T) and CASPT2 simulations were performed using Molpro 2010.<sup>47</sup>

## 2.3 Kinetic modeling

The development of the kinetic model was performed by following a hierarchical and modular approach, as originally conceived in the CRECK kinetic framework.<sup>48</sup> The core H<sub>2</sub>/O<sub>2</sub> mechanism was adopted after the work of Metcalfe et al.<sup>49</sup> The NO<sub>x</sub> module, foundation of the whole NH<sub>3</sub> mechanism, was taken from the work of Song et al.,<sup>38</sup> on turn based on the works of Faravelli, Frassoldati et al.<sup>50,51</sup> The major updates were performed on HONO/HNO<sub>2</sub> chemistry, after the recent work of Chen et al.<sup>52</sup> For all the species, the thermodynamic properties were systematically updated using the database of Burcat and Ruscic.<sup>53</sup>

Ammonia submechanism was added on top of the NO<sub>x</sub> module, and the critical reactions are summarized in Table 1. The parameters of reactions R1 to R6 and R28 were calculated through the fitting of the temperature-dependent rates obtained from the related theoretical calculations via a modified-Arrhenius format  $k = AT^\beta \exp[-E_{act}/(RT)]$ . In addition to the dissociation reaction calculated in this work, the reactions involving NH and NH<sub>2</sub> radicals were taken from Klippenstein et al.,<sup>21</sup> as well as NH<sub>2</sub>OH chemistry. The only exception is represented by R7: in this case, the high-temperature estimation of Davidson et al.<sup>12</sup> was adopted (~35% smaller), which (extrapolated) showed a better agreement with lower-temperature experimental data. As for NH<sub>2</sub> reactions with NO and NO<sub>2</sub> (R16–R19), both rate constants and branching ratios between the product channels were taken following the guidelines of Glarborg et al.,<sup>31</sup> while for NH + NO (R26 and R27), the theoretical calculations of Haworth et al.<sup>54</sup> were fitted in the 1000–2600 K interval. For the higher N<sub>2</sub>H<sub>x</sub> chemistry, reactions were mainly taken from the review of Dean and Bozzelli,<sup>55</sup> including H-abstractions from N<sub>2</sub>H<sub>x</sub> compounds and N<sub>2</sub>H<sub>x</sub> dissociation.

Table 1 - List of critical reactions in the NH<sub>3</sub> oxidation mechanism. Reaction rate expression is modified Arrhenius  $k = AT^\beta \exp[-E_{act}/(RT)]$ . Units are cm<sup>3</sup>, cal, mol, K

ID	Reaction	A	$\beta$	$E_{act}$	Notes	Ref
R1	NH <sub>3</sub> ↔ NH <sub>2</sub> + H	7.230E+29	-5.316	110862.4	0.1 atm	PW
		3.497E+30	-5.224	111163.3	1 atm	
		1.975E+31	-5.155	111887.8	10 atm	
		2.689E+31	-4.920	112778.7	100 atm	
R2	NH <sub>3</sub> +H ↔ NH <sub>2</sub> +H <sub>2</sub>	1.963E+04	2.854	8520.2		PW
R3	NH <sub>3</sub> +OH ↔ NH <sub>2</sub> +H <sub>2</sub> O	1.559E+05	2.372	118.9		PW
R4	NH <sub>3</sub> +O ↔ NH <sub>2</sub> +OH	4.430E+02	3.180	6739.9		PW
R5	NH <sub>3</sub> +HO <sub>2</sub> ↔ NH <sub>2</sub> +H <sub>2</sub> O <sub>2</sub>	1.173E+00	3.839	17260.0		PW
R6	NH <sub>3</sub> +O <sub>2</sub> ↔ NH <sub>2</sub> +HO <sub>2</sub>	1.415E+10	1.285	55224.0		PW
R7	NH <sub>2</sub> +NH ↔ N <sub>2</sub> H <sub>2</sub> +H	1.500E+15	-0.500	0.0		12
R8	NH <sub>2</sub> +NH ↔ NH <sub>3</sub> +N	9.600E+05	2.460	107.0		21

R9	NH+NH $\leftrightarrow$ NH <sub>2</sub> +N	5.700E-01	3.880	342.0		21
R10	NH+NH $\rightarrow$ N <sub>2</sub> +H <sub>2</sub>	6.260E+12	-0.036	-160.9		21
R11	NH+NH $\rightarrow$ N <sub>2</sub> +H+H	5.634E+13	-0.036	-160.9		21
R12	NH <sub>2</sub> +NH <sub>2</sub> $\leftrightarrow$ NH <sub>3</sub> +NH	5.640E+00	3.530	550.0		21
R13	NH <sub>2</sub> +O <sub>2</sub> $\leftrightarrow$ HNO+OH	2.900E-02	3.764	18185.0		22
R14	NH <sub>2</sub> +O <sub>2</sub> $\leftrightarrow$ H <sub>2</sub> NO+O	2.600E+11	0.487	29050.0		22
R15	NH <sub>2</sub> +HO <sub>2</sub> $\leftrightarrow$ OH+H <sub>2</sub> NO	1.566E+13	0.000	0.0		58
R16	NH <sub>2</sub> +NO $\leftrightarrow$ N <sub>2</sub> +H <sub>2</sub> O	2.600E+19	-2.369	870.0		19
R17	NH <sub>2</sub> +NO $\leftrightarrow$ NNH+OH	4.300E+10	0.294	-866.0		19
R18	NH <sub>2</sub> +NO <sub>2</sub> $\leftrightarrow$ H <sub>2</sub> NO+NO	8.600E+11	0.110	-1186.0		31
R19	NH <sub>2</sub> +NO <sub>2</sub> $\leftrightarrow$ N <sub>2</sub> O+H <sub>2</sub> O	2.200E+11	0.110	-1186.0		31
R20	NH <sub>2</sub> +H $\leftrightarrow$ NH+H <sub>2</sub>	4.000E+13	0.000	3650.0		12
R21	NH <sub>2</sub> +OH $\leftrightarrow$ NH+H <sub>2</sub> O	9.600E+06	1.970	670.0		59
R22	NH <sub>2</sub> +O $\leftrightarrow$ NH+OH	7.000E+12	0.000	0.000		55
	duplicate	3.300E+08	1.500	5076.8		55
R23	NH <sub>2</sub> +O $\leftrightarrow$ HNO+H	1.500E+15	-0.547	836.7		60
	duplicate	7.730E+13	-0.277	646.4		60
R24	NH+O <sub>2</sub> $\leftrightarrow$ HNO+O	4.050E+11	0.090	10670.0		61
R25	NH+O <sub>2</sub> $\leftrightarrow$ NO+OH	2.010E+15	-1.380	5670.0		61
R26	NH+NO $\leftrightarrow$ N <sub>2</sub> O+H	5.328E+12	0.026	-2893.9		54
R27	NH+NO $\leftrightarrow$ N <sub>2</sub> +OH	3.635E+10	0.361	-2844.3		54
R28	HNO $\leftrightarrow$ H+NO	2.104E+20	-3.151	48651.0	0.1 atm	PW
		1.568E+21	-3.113	48707.0	1 atm	
		1.060E+22	-3.059	48978.0	10 atm	
		4.976E+22	-2.963	49471.0	100 atm	
R29	HNO+O <sub>2</sub> $\leftrightarrow$ NO+HO <sub>2</sub>	2.000E+13	0.000	14896.0		55
R30	H <sub>2</sub> NO+H $\leftrightarrow$ HNO+H <sub>2</sub>	4.800E+08	1.500	1559.8		55
R31	H <sub>2</sub> NO+H $\leftrightarrow$ NH <sub>2</sub> +OH	4.000E+13	0.000	0.000		55
R32	H <sub>2</sub> NO+O $\leftrightarrow$ HNO+OH	3.300E+08	1.500	486.8		55
R33	H <sub>2</sub> NO+OH $\leftrightarrow$ HNO+H <sub>2</sub> O	2.400E+06	2.000	1192.2		55
R34	H <sub>2</sub> NO+NO <sub>2</sub> $\leftrightarrow$ HNO+HONO	6.000E+11	0.000	2000.0		57
R35	H <sub>2</sub> NO+NH <sub>2</sub> $\leftrightarrow$ HNO+NH <sub>3</sub>	1.800E+06	1.940	-580.0		55
R36	H <sub>2</sub> NO+O <sub>2</sub> $\leftrightarrow$ HNO+HO <sub>2</sub>	2.300E+02	2.994	16500.0		31,36
R37	H <sub>2</sub> NO+HO <sub>2</sub> $\leftrightarrow$ HNO+H <sub>2</sub> O <sub>2</sub>	3.360E+05	2.000	-1434.0	estimated	PW

At low temperatures ( $T < 1200$  K), different works<sup>31,33,34</sup> highlighted the importance of H<sub>2</sub>NO and HNO as key species. H<sub>2</sub>NO is mainly formed from NH<sub>2</sub> interaction with O<sub>2</sub> and oxygenated species like HO<sub>2</sub> and NO<sub>2</sub>. The delicate competition between the different H-abstraction reactions on H<sub>2</sub>NO drives the reactivity of the whole system, since abstraction by O<sub>2</sub> giving HNO and HO<sub>2</sub> (R32) activates the radical branching, while the remaining abstractors deplete H<sub>2</sub>NO and hinder the branching process. Among them, the only reaction studied at a fundamental level is R36,<sup>36</sup> included by Glarborg et al. in their review<sup>31</sup> (as well as in the present work) with an activation energy lowered by 2.5 kcal mol<sup>-1</sup>. Under the investigated conditions, the low temperature and high oxygen concentration resulting in high amounts of HO<sub>2</sub> make the related H-abstraction (R37) particularly important. Considering the known kinetic parameters evaluated for the H-abstraction by O<sub>2</sub>, H-abstraction via HO<sub>2</sub> was estimated following the generalized methodology proposed by Ranzi et al.<sup>56</sup> to predict kinetic parameters for H-abstraction reactions from hydrocarbons. The obtained constant has a comparable activation energy to that proposed by Dean and Bozzelli,<sup>55</sup> but on average it is a factor  $\sim 9$  smaller on a  $T = 500$ – $1500$  K interval. The remaining H-abstractions from H<sub>2</sub>NO (R30–R35) were taken from the evaluations of

Dean and Bozzelli,<sup>55</sup> or estimations from Glarborg et al.<sup>57</sup> Due to the high sensitivity of NH<sub>3</sub> reactivity to the H<sub>2</sub>NO amount at low temperatures, an accurate evaluation of the remaining H-abstractions can be a useful development of this activity; this is especially true in relation to the most stable radicals (i.e. NH<sub>2</sub>, NO<sub>2</sub>) at low temperatures, for which Ranzi et al.<sup>56</sup> did not propose any correlation.

The complete kinetic mechanism is made up of 31 species and 203 reactions, and is provided as Supplementary Material of this work in CHEMKIN format, together with thermodynamic and transport properties.

### 3. Results and discussion

#### 3.1. Estimated rate constants

The rate constant of two barrierless decomposition reactions and five H-abstraction reactions were determined theoretically. In particular, the barrierless decomposition of ammonia into NH<sub>2</sub> + H and of HNO into NO + H were determined as a function of temperature and pressure solving the master equation, and then fitted in the PLOG format. Ammonia decomposition has been studied in literature both as a forward and backward (recombination) process. The high-pressure rate constant calculated in the present work for ammonia recombination has a slight temperature dependence, increasing from  $1.7 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  to  $2.8 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  going from 300 K to 2500 K. These values are in reasonable agreement with the temperature independent value  $1.6 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  suggested by Glarborg et al.<sup>31</sup> The pressure-dependent decomposition rate is deep in its fall-off regime, so that the calculations are significantly affected by the inter molecular collisional energy transfer model adopted in the ME simulations. The experimental literature reports either experimental measurements of ammonia decomposition at high temperatures (higher than 2000 K)<sup>12,58</sup> or of NH<sub>2</sub> + H recombination rates at room temperature, but a systematic temperature- and pressure-dependent study is not available to the authors' knowledge.<sup>62,63</sup> In order to fit both high- and low-temperature data sets, a single exponential energy transfer model was adopted, with a  $\Delta E_{\text{down}}$  of  $130 (T[\text{K}]/298)^{0.8} \text{ cm}^{-1}$ . At 1 atm, the calculated rate constant is about a factor of 2 slower than the Davidson et al.<sup>12</sup> high temperature experimental decomposition rate, a factor of 2 larger than the high-temperature Baulch recommendation,<sup>58</sup> and in excellent agreement with the recent recombination measurement of Altinay and MacDonald,<sup>63</sup> on whose data  $\Delta E_{\text{down}}$  was fitted in the present study. Experimental and theoretical data are compared in Figure 4.

The rate constant for HNO decomposition was determined using the same  $\Delta E_{\text{down}}$  value used for NH<sub>3</sub>. The calculated high-pressure H + NO recombination rate is comprised between  $2.3 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $1.9 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  in the 300–2500 K range, thus in reasonably good agreement with the recommendation of Tsang and Herron<sup>64</sup> (between  $1.2 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $0.6 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ), which has a large uncertainty factor of 5. The low-pressure recombination rate constant is compared with experimental data in Figure 5. While the experimental data at room temperature are slightly overestimated, the agreement at temperatures higher than 500 K is quite good and fits very

well with the data of Glarborg et al.,<sup>65</sup> which suggests that the pressure dependence is well caught by the adopted energy transfer model.

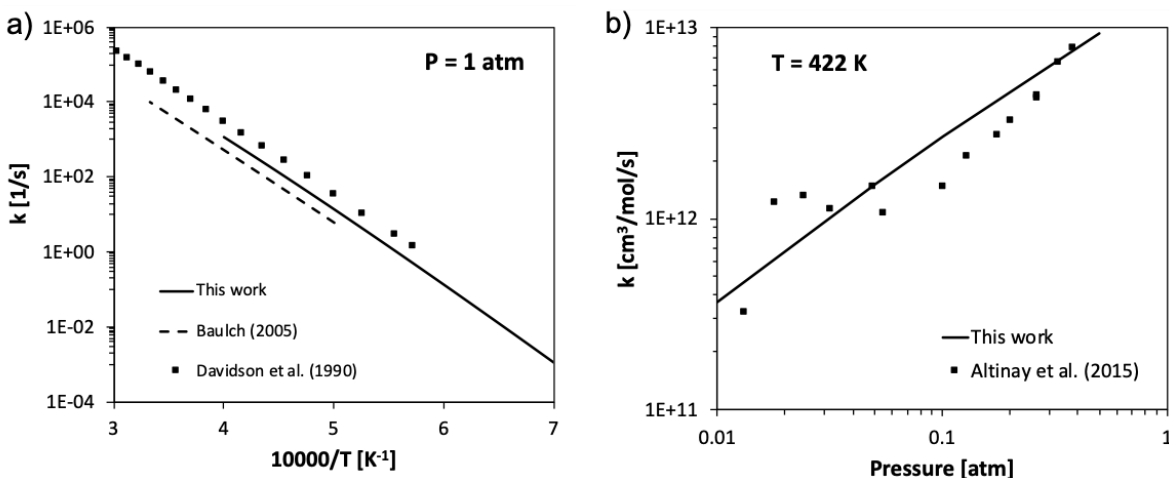


Figure 4 - Rate constant calculated a) for ammonia decomposition at 1 atm and b)  $\text{NH}_2 + \text{H}$  recombination at 422 K compared with experimental data.<sup>12,58,63</sup>

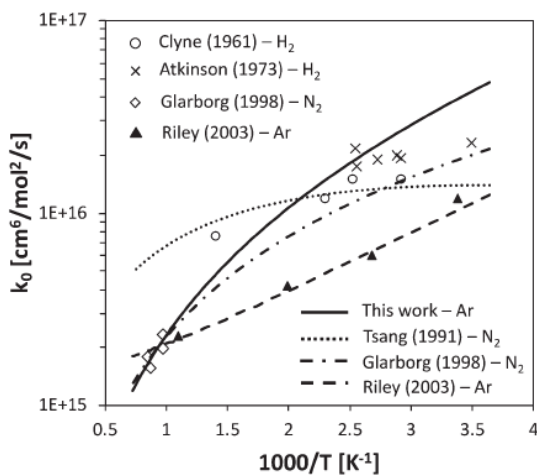


Figure 5 - Low-P recombination rate constant of the  $\text{H} + \text{NO}$  reaction, for different bath gases, compared with selected literature data.<sup>64-68</sup>

Rate constants were calculated for the five H-abstraction reactions from  $\text{NH}_3$  by H, OH, O(<sup>3</sup>P), HO<sub>2</sub>, and O<sub>2</sub>. The calculated abstraction rate constants are in general within a factor of 2 from experimental measurements, when available. This is for example the case for H-abstraction by H, where the calculated rate constant is about a factor of 1.7 larger than that measured by Sutherland and Klemm<sup>69</sup> and Sutherland and Michael,<sup>11</sup> in the 750–1770 K temperature range. Also in the case of H-abstraction by OH, the agreement with literature data is quite good,<sup>70-72</sup> well within a factor of 2, as shown in Figure 6. The energy barrier calculated at the CASPT2 level is 2.2 kcal mol<sup>-1</sup>, thus about 1 kcal mol<sup>-1</sup> smaller than the 3.2 kcal mol<sup>-1</sup> determined at the CCSD(T) level, which is consistent with the

multireference character of this reaction. A larger disagreement is observed for H-abstraction by O(<sup>3</sup>P). The calculated rate constant underestimates the experimental measurements of Sutherland et al.<sup>73</sup> by about a factor of 2.7 at 800 K. However, the disagreement decreases significantly with temperature, becoming just a factor of 1.2 at 1500 K. This suggests that the calculated energy barrier is probably overestimated, as was also suggested by Klippenstein et al.<sup>21</sup> in the study of this reaction channel for their CCSD(T) level energy barrier. It should be noted that, for this reaction channel, the electronic degeneracy of the transition state was assumed to be 6, as the ground and excited state in O(<sup>3</sup>P) abstraction reactions are nearly degenerate, as observed in a recent study of this reaction class.<sup>74</sup>

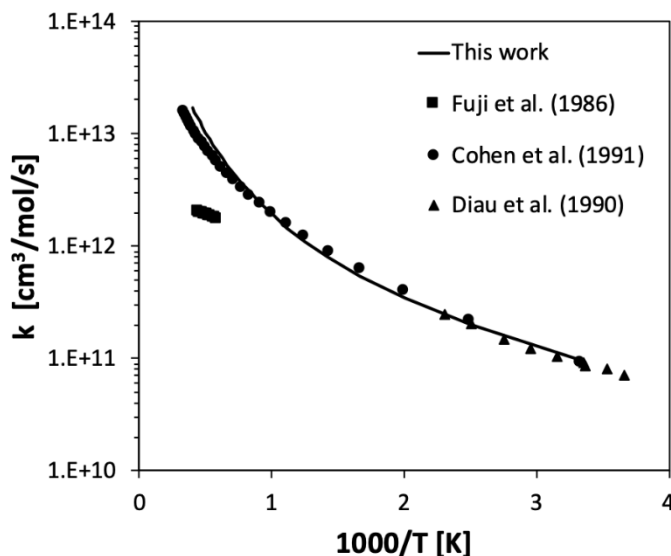


Figure 6 - Rate constant calculated for H-abstraction by OH on NH<sub>3</sub> compared with selected experimental data.<sup>70-72</sup>

For the H-abstraction channels by HO<sub>2</sub> and O<sub>2</sub>, no literature reference is available, so that it is difficult to estimate their uncertainty. The rate constant estimation protocol adopted here is essentially the same as used in the ESTokTP benchmark study,<sup>44</sup> where it was found that for abstraction reactions the uncertainty was smaller than a factor of 2 when compared to a large experimental data set. Considering the multireference character of several of the investigated reactions, it is though reasonable to assume that, under combustion conditions, the uncertainty factor of these rates may be up to a factor of 3.

For H-abstraction from NH<sub>3</sub> by O<sub>2</sub>, previous works are available on the reverse reaction rate constant, below 500 K (Figure 7). The photochemical study of Sarkisov et al.<sup>75</sup> estimated an overall rate coefficient of  $4.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the reaction  $\text{NH}_2 + \text{HO}_2 \rightarrow \text{products}$  at 300 K, while Baulch et al.<sup>76</sup> recommended a value of  $1.6 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  between 300 K and 400 K. The fit of the reverse H-abstraction obtained in this work overestimates the value of Sarkisov et al.<sup>75</sup> at room temperature by a factor of 2. Anyway, the previous evaluations of Dean and Bozzelli<sup>55</sup> and Sumathi et al.<sup>77</sup> underestimate the low-temperature data by orders of magnitude. This confirms the significant

uncertainty existing in the theoretical evaluation of such an important step in the NH<sub>3</sub> oxidation mechanism.

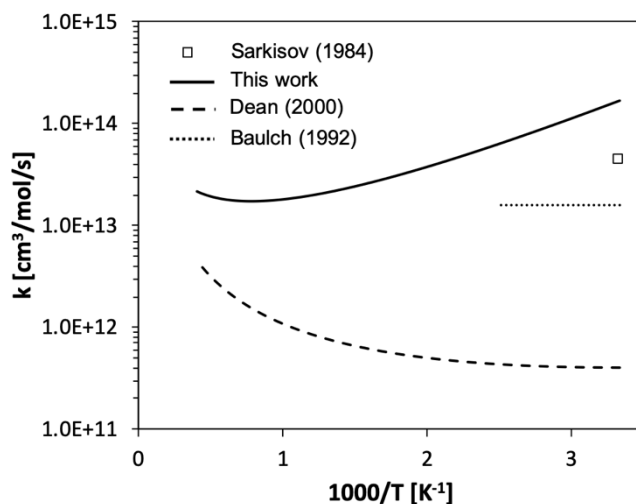


Figure 7 - Comparison between calculated rate constant and literature data<sup>55,75,76</sup> for reverse H-abstraction by O<sub>2</sub> on NH<sub>3</sub>.

The calculated rate constants are included in Table 1 and in the CHEMKIN format as Supplementary Material to this paper. Input files for the MESS calculations, thus inclusive of energy barriers, stationary points geometries, and of the variational analysis results are also reported as Supplementary Material.

### 3.2. NH<sub>3</sub> oxidation: experiments and kinetic analysis

The gas-phase oxidation of ammonia was investigated under a wide range of operating conditions: following a hierarchical approach, pyrolysis conditions were first considered, followed by high-temperature ( $T$ ) oxidation, then intermediate- and low-temperatures with variable pressure ( $P$ ), residence time ( $\tau$ ) and equivalence ratio ( $\Phi$ ), as shown in Table 2. In the following, the new experimental results collected in jet stirred and flow reactors are shown, and analyzed using the newly-developed kinetic model in order to explain the dynamics of conversion from NH<sub>3</sub> to final products. The full validation of the mechanism against the case studies listed in Table 2 is provided in the Supplementary Material. For the sake of compactness, only selected cases are analyzed and discussed to highlight the main features of ammonia.

Table 2 - Configurations and operating conditions investigated for NH<sub>3</sub> pyrolysis and oxidation

System	Composition	Operating conditions	$T$	$P$	Reference
JSR	NH <sub>3</sub> /O <sub>2</sub> /He	500 ppm NH <sub>3</sub> / $\Phi = 0.1 - 0.2$ / $\tau = 1.5$ s	500 - 1200 K	106.7 kPa	PW
	NH <sub>3</sub> /NO/O <sub>2</sub> /He	500-1000 ppm NH <sub>3</sub> / 500-1000 ppm NO / $\Phi = 0.1 - 2$ / $\tau = 0.1$ s	1100 - 1450 K	1 atm	78

	NH <sub>3</sub> /NO/O <sub>2</sub> /N <sub>2</sub>	960-10800 ppm NH <sub>3</sub> / 400-3000 ppm NO / O <sub>2</sub> = 0.8-6% / $\tau = 374/T[K] \text{ s}$	950 - 1450 K	1 atm	79
FR	NH <sub>3</sub> /O <sub>2</sub> /He	1000 ppm NH <sub>3</sub> / $\Phi = 0.375$ / $\tau = 50 \text{ ms}$	1200 - 2000 K	126.7 kPa	PW
	NH <sub>3</sub> /O <sub>2</sub> /N <sub>2</sub>	242 ppm NH <sub>3</sub> / O <sub>2</sub> = 10% / $\tau = 339/T[K] \text{ s}$	850 - 1250 K	1 atm	35
	NH <sub>3</sub> /O <sub>2</sub> /N <sub>2</sub>	729 ppm NH <sub>3</sub> / $\Phi = 1.23$ / variable $\tau$	450 - 925 K	30 - 100 bar	36
	NH <sub>3</sub> /O <sub>2</sub> /N <sub>2</sub>	800 ppm NH <sub>3</sub> / 2.5 % O <sub>2</sub> / $\tau = 71/T[K] \text{ s}$	950 - 1350 K	1.05 bar	80
	NH <sub>3</sub> /Ar	2700 - 3000 ppm NH <sub>3</sub>	2300 - 2800 K	0.8 - 1.1 atm	12
ST	NH <sub>3</sub> /O <sub>2</sub> /Ar	Ar = 98-99% / $\Phi = 0.5 - 2$	1550 - 2500 K	1.4 - 30 atm	27
	NH <sub>3</sub> /N <sub>2</sub> /O <sub>2</sub>	N <sub>2</sub> /O <sub>2</sub> = 3.76:1 / $\Phi = 0.5 - 2$	1100 - 1600 K	20 - 40 bar	32
	NH <sub>3</sub> /O <sub>2</sub> /N <sub>2</sub> /Ar	5-12% NH <sub>3</sub> / $\Phi = 0.2 - 0.5$	1000 - 1100 K	37 - 75 atm	33
RCM	NH <sub>3</sub> /O <sub>2</sub> /Ar	$\Phi = 0.5 - 2$ / 70 % Ar	1000 - 1130 K	40 - 60 bar	34
LFS	NH <sub>3</sub> /N <sub>2</sub> /O <sub>2</sub>	$\Phi = 0.7 - 1.65$	298 K	1 atm	81
	NH <sub>3</sub> /O <sub>2</sub>	$\Phi = 0.2 - 2$	298 K	1 atm	82
	NH <sub>3</sub> /N <sub>2</sub> /O <sub>2</sub>	$\Phi = 0.6 - 1.5$ / 21 - 45 % O <sub>2</sub>	298 K	1 - 5 atm	83
BSF	NH <sub>3</sub> /O <sub>2</sub>	40 - 65% NH <sub>3</sub> - Balance O <sub>2</sub> / $v = 60.5 \text{ cm/s}$	300 K	20 torr	84

### 3.2.1. Jet stirred reactor

Experiments for NH<sub>3</sub> oxidation in JSR were carried out with helium as bath gas, by oxidizing 500 ppm of ammonia with 2% and 4% oxygen, respectively. Considering a global reaction  $4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$ , the corresponding  $\Phi$  values are 0.0188 and 0.0093. Results are shown in Figure 8, with regard to NH<sub>3</sub> and NO mole fractions. NO<sub>2</sub> was not experimentally detected, in agreement with the simulations predicting maximum values of  $\sim 1.5$  ppm.

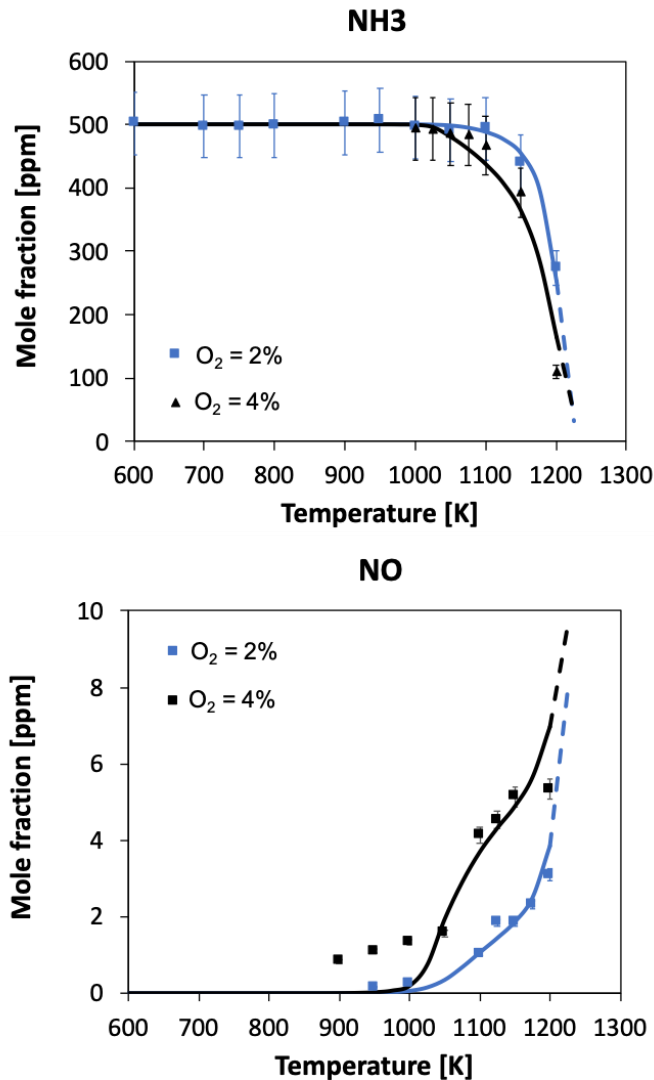


Figure 8 - Oxidation of 500 ppm of NH<sub>3</sub> in a JSR. Experimental and modeling results.  $P = 800$  torr.  $\tau = 1.5$  s. Dashed lines: model extrapolation beyond the maximum reactor temperature.

Considering the highest oxygen concentrations, the reaction starts at relatively high temperatures, i.e. 1100 K and 1025 K with 2% and 4% oxygen, respectively. In both cases, the increase in consumption rate is very slow with temperature but it is opposite to the amount of oxygen: in the 4% case, initial NH<sub>3</sub> is halved after 150 K from the reactivity onset, while in the 2% case this occurs after 100 K from the start of consumption. The kinetic model is able to predict this behavior, and at temperatures higher than 1200 K, it predicts a higher conversion with 2% oxygen. No experimental data are available beyond  $T = 1200$  K due to the mechanical resistance of the quartz reactor, but the trend before the maximum allowed temperature also suggests an inversion in reactivity. A satisfactory agreement can also be seen in NO prediction, although the experiments detect an earlier formation of NO with 4% oxygen ( $\sim 1$  ppm at  $T = 900$  K, where NH<sub>3</sub> conversion is close to zero). The shape of both profiles is well predicted by the kinetic model: in particular, at higher temperatures NO yield is predicted to converge to comparable values, i.e. 2% of the initial nitrogen amount.



Interestingly, with 4% O<sub>2</sub> the NO profile is predicted having a double inflection point, and this is also confirmed by experimental results.

In order to identify the different reaction pathways leading to NH<sub>3</sub> conversion and NO formation, reaction flux analyses were performed for two representative conditions, i.e. T = 1050 K and T = 1200 K with 4% initial oxygen, when NH<sub>3</sub> conversion is ~10% and ~70%, respectively. The diagrams shown in Figure 9 highlight similarities and differences between the two cases.

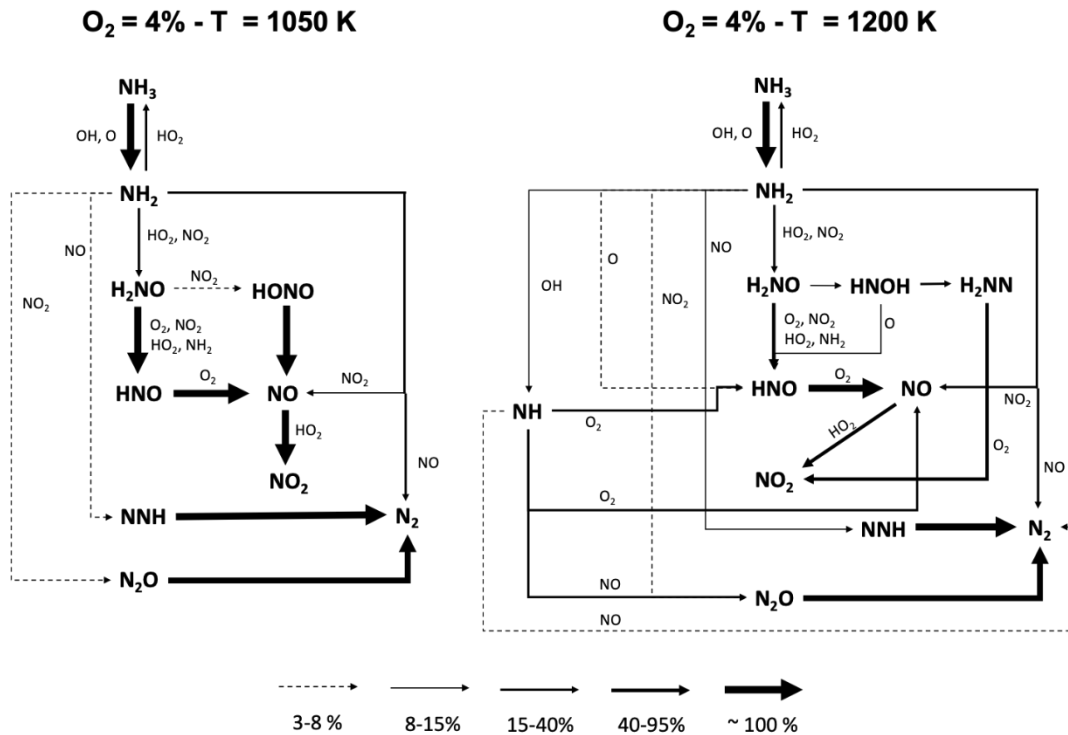


Figure 9 - Reaction flux analysis at different temperatures. Flux intensity is relative to the single molecule. For the sake of clarity, reactions between two N-molecules are reported only once.

The major paths converting NH<sub>3</sub> into N<sub>2</sub> pass through NH<sub>2</sub> interaction with NO via R16 and R17 product channels, the latter forming NNH on turn quickly decomposing to N<sub>2</sub>. NO formation is governed by the formation of H<sub>2</sub>NO via NH<sub>2</sub> reaction with HO<sub>2</sub> and NO<sub>2</sub>, respectively. H<sub>2</sub>NO is then oxidized to HNO and finally to NO (with a small fraction passing through HONO and its further decomposition). At T = 1050 K, the higher amounts of NO<sub>2</sub> caused by the abundance of HO<sub>2</sub> radicals in the system enhance NH<sub>2</sub> conversion via the two channels of the NH<sub>2</sub> + NO<sub>2</sub> reaction (R18 and R19), and promote an earlier reactivity. On the other hand, the presence of HO<sub>2</sub> radical has a further effect: the flux analysis shows that the initiation reaction R6 is actually reversed, i.e. it behaves like a termination. Therefore, since a higher O<sub>2</sub> concentration results in a higher HO<sub>2</sub> amount, the increase in reactivity with 4% initial O<sub>2</sub> is slower with temperature, until the mixture with 2% O<sub>2</sub> becomes more reactive.

At higher temperatures, several major differences must be pointed out. First of all, the smaller amounts of HO<sub>2</sub> radicals result in lower NO<sub>2</sub> mole fractions. Therefore, NH<sub>2</sub> + NO prevails over NH<sub>2</sub> + NO<sub>2</sub>, and the relative weight of the branching channel R17 increases. Moreover, the high-temperature chemistry of NH<sub>3</sub> becomes important: the significant presence of OH and O opens new pathways, forming NH radical (R21) and HNO (R23), respectively. The former reacts with NO forming N<sub>2</sub> (R26 and R27), either directly or via N<sub>2</sub>O, while its oxidation with O<sub>2</sub> (R24 and R25) ultimately forms NO, whether or not passing through HNO. On the other hand, the reaction with O (R23) allows bypassing the H<sub>2</sub>NO intermediate in the NH<sub>3</sub> oxidation pathway, in such a way that H<sub>2</sub>NO becomes less and less important at higher temperatures.

The described picture is further confirmed by the sensitivity analysis of NH<sub>3</sub> mole fraction, used as representative of the system reactivity. Results are shown in Figure 10 for two representative conditions, chosen such that a comparable conversion is attained (~10%).

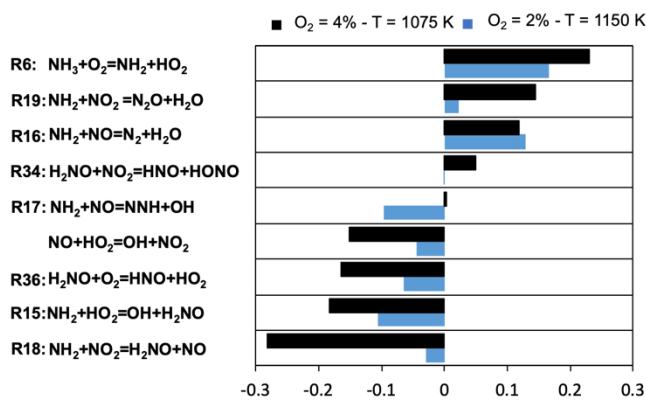


Figure 10 - Sensitivity coefficients to NH<sub>3</sub> mole fraction in two representative conditions of JSR experiments.

Apparently, the system is controlled by the reactions involving HO<sub>2</sub> radicals, and for them, sensitivity coefficients are higher in the O<sub>2</sub> = 4% case. The H-abstraction by O<sub>2</sub> (R6), in spite of formally being an initiation, actually slows down the reactivity to a significant extent. Indeed, as shown in Figure 9, R6 rather behaves as a termination step due to the high amounts of HO<sub>2</sub> and NH<sub>2</sub> radicals. On the other hand, H<sub>2</sub>NO formation (R15) and successive oxidation (R36) enhance the overall reactivity. With 4% O<sub>2</sub>, the NO<sub>2</sub> channels become critical in regulating NH<sub>3</sub> consumption: the formation of H<sub>2</sub>NO (R18) gives a substantial contribution to the oxidation path (while a contrasting action is played by the termination channel R19). For this reason, the conversion of NO to NO<sub>2</sub> via HO<sub>2</sub> boosts NH<sub>3</sub> conversion. Indeed, the branching channel via NO (R17) becomes significant only at higher temperatures, as it can be noticed from the higher sensitivity coefficient of R17 in the O<sub>2</sub> = 2% case. In parallel, the channels involving NO<sub>2</sub> lose their crucial role with increasing temperature. Finally, the slowing effect of the remaining H-abstractions on H<sub>2</sub>NO (especially NO<sub>2</sub>) can be noticed especially at the lowest temperatures, because of the removal of active radicals from the low-temperature oxidation path.

Further examples of  $\text{NH}_3$  oxidation in JSRs at atmospheric pressure can be found in the Supplementary Material where in particular the enhancing effect of  $\text{NO}$  addition is highlighted and the thermal DeNO<sub>x</sub> model is validated.

### 3.2.2. Flow reactor

Moving to higher temperatures, ammonia oxidation was then studied in a FR at temperatures above 1300 K. Experiments were carried out by injecting 1000 ppm  $\text{NH}_3$  with 2000 ppm  $\text{O}_2$  ( $\Phi = 0.375$ ), with a flow rate regulated in such a way to obtain a fixed residence time in the reactive zone, equal to 50 ms. Numerical simulations were performed by imposing the experimental temperature profile, and a variable flow rate (according to the set-point temperature) within the reactor. Figure 11 shows the results for the major species. Ammonia conversion starts at around  $T = 1400$  K, and is complete above 1500 K. In this temperature interval,  $\text{H}_2$  is formed as an intermediate product, with an observed peak of about 50 ppm.  $\text{N}_2$  and  $\text{NO}$  are the major nitrogenated products, with the  $\text{NO}$  yield progressively increasing with temperature.

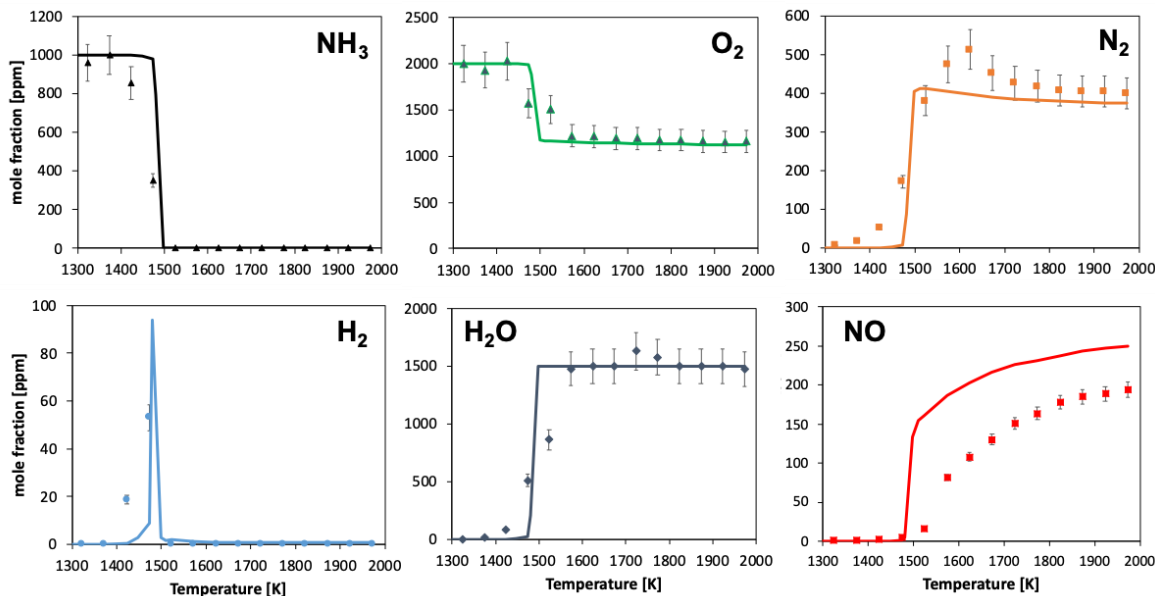


Figure 11 - Oxidation of 1000 ppm  $\text{NH}_3$  with 2000 ppm  $\text{O}_2$  in a FR. Experimental and modeling results.  $P = 950$  torr. Average  $\tau$  in the reactive zone is 50 ms.

The kinetic model predicts the ignition temperature reasonably well, and consequently  $\text{NH}_3$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$  profiles. Anyway, the predicted consumption rate of ammonia and product formation is more abrupt than what was experimentally observed. The location of the  $\text{H}_2$  peak is satisfactorily caught. The onset of  $\text{NO}$  formation is well reproduced in terms of temperature. However, the predicted  $\text{NO}/\text{N}_2$  ratio is higher than the measured one: the shape of both profiles is well caught, but an overestimation of the  $\text{NO}$  mole fraction (about 20%) is observed at high-temperature.

Figure 12 shows the routes leading to NO and N<sub>2</sub> formation at intermediate temperatures (i.e. straight after the reactivity onset). Compared to JSR, the pyrolysis mechanism plays a major role. The formation of N<sub>2</sub>H<sub>2</sub> via R7 opens a new branching route through NNH, since overall an H atom is released in the conversion from NH<sub>2</sub> to N<sub>2</sub> (2 if N<sub>2</sub>H<sub>2</sub> undergoes decomposition). The second branching route passes through HNO formation via NH<sub>2</sub> + O (R23), then releasing NO as final product.

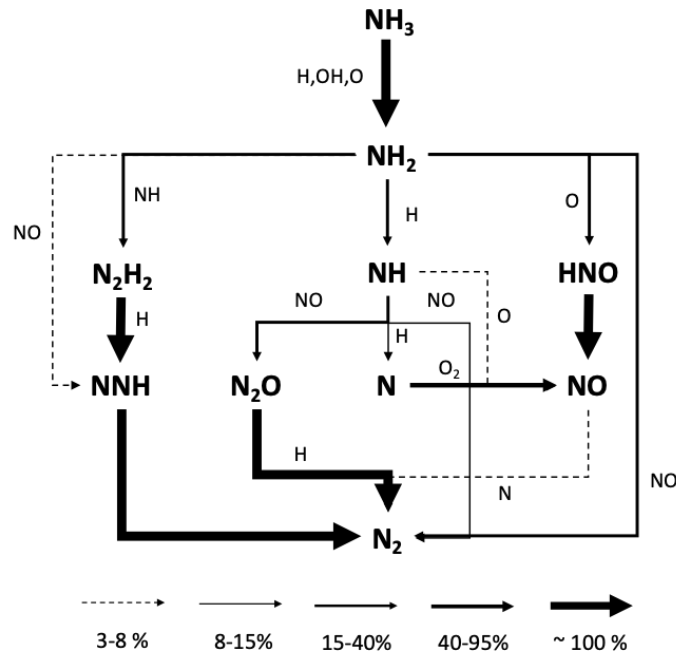


Figure 12 - Reaction flux analysis in FR at  $T = 1523$  K and at a reactor length of 55 cm. Flux intensity is relative to the single molecule. For the sake of clarity, reactions between two N-molecules are reported only once.

The competition between the two paths becomes more apparent in the sensitivity analysis shown in Figure 13, performed right after the reactivity onset, at a reactor length where NH<sub>3</sub> is almost fully consumed, and the reactions driving NO/N<sub>2</sub> selectivity can be distinguished. It can be observed that under such conditions, the path via HNO (R23 and R28) controls NO formation more than the path via N (thermal NO<sub>x</sub>). On the other side, the major antagonists to NO selectivity are its reactions with NH and NH<sub>2</sub>, respectively (R27 and R16), directly converting into N<sub>2</sub>. Moreover, a higher formation of NH<sub>2</sub> (R3), precursor to the formation of both NO and N<sub>2</sub>, enhances the formation of N<sub>2</sub> while having an antagonistic effect on NO. This can be attributed to the combination of higher thermal DeNO<sub>x</sub> effects (R16) and NH formation via R20, on turn reacting again with NO and providing N<sub>2</sub>.

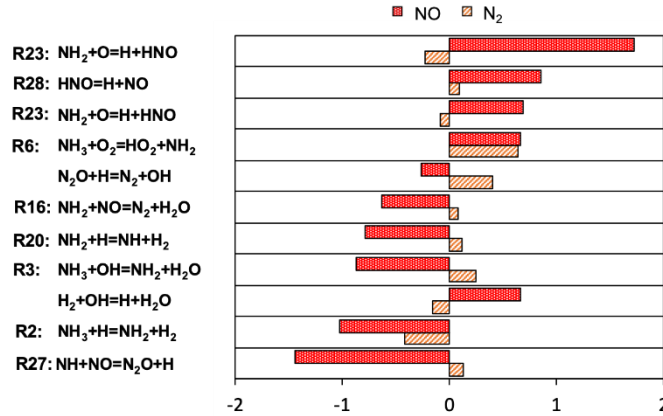


Figure 13 - Sensitivity coefficients to NO and N<sub>2</sub> mole fractions in FR case evaluated at  $T = 1523$  K and at a reactor length of 58.5 cm ( $\sim 100\%$  ammonia conversion).

### 3.2.3. Ignition delay times

The prediction ability of the kinetic model was assessed for the measurement of ignition delay times (IDTs) in a wide range of operating conditions, i.e.  $1000 \text{ K} < T_c < 2500 \text{ K}$  and  $1.4 \text{ atm} < P_c < 60 \text{ atm}$ , with different dilution levels. Due to the low reactivity of ammonia and longer IDTs, the presence of non-ideal, dynamic effects must be taken into account in the simulation of experimental data at both intermediate- and low-temperature conditions. Therefore, for the intermediate-temperature shock tube (ST) measurements,<sup>32</sup> the experimental pressure profile of the single experiments was converted into volume profile, starting from the arrival time of the reflected shock wave until the time point equal to 90% of the measured IDT, after which the volume was kept constant. Constrained-volume 0D simulations were then performed using the obtained profile. For the rapid compression machine (RCM) simulations,<sup>34</sup> the whole recorded pressure profile was converted into volume profile and used to perform constrained-volume 0D simulations. High-temperature datasets were instead simulated as homogeneous constant-volume 0D simulations.

Figure 14 shows the results of 3 different equivalence ratios at various pressures. A satisfactory agreement can be observed for the high-temperature data of Mathieu and Petersen<sup>27</sup> in the whole operating range, with a slight underprediction under lean conditions. At intermediate temperatures ( $1100 \text{ K} < T_c < 1600 \text{ K}$ ), the mechanism well reproduces the non-linear behavior of experimental data, due to pre-ignition effects. More significant deviations are can be seen at  $\Phi = 2$  and  $P_c = 40$  bar. Yet, especially at the lowest temperatures ( $\sim 1100 \text{ K}$ ), the experimental points at  $P_c = 20$  and 40 bar are essentially overlapped. It must be also pointed out that the strongly irregular trend observed under stoichiometric and rich conditions is due to the different individual pressure histories recorded for the single points, which were used for the numerical simulations. The most critical predictions are observed at the lowest temperatures, i.e. when simulating RCM data by He et al.<sup>34</sup> where ignition is slightly underestimated at  $\Phi = 0.5$ , and overestimated at  $\Phi = 1$  and especially  $\Phi = 2$ .

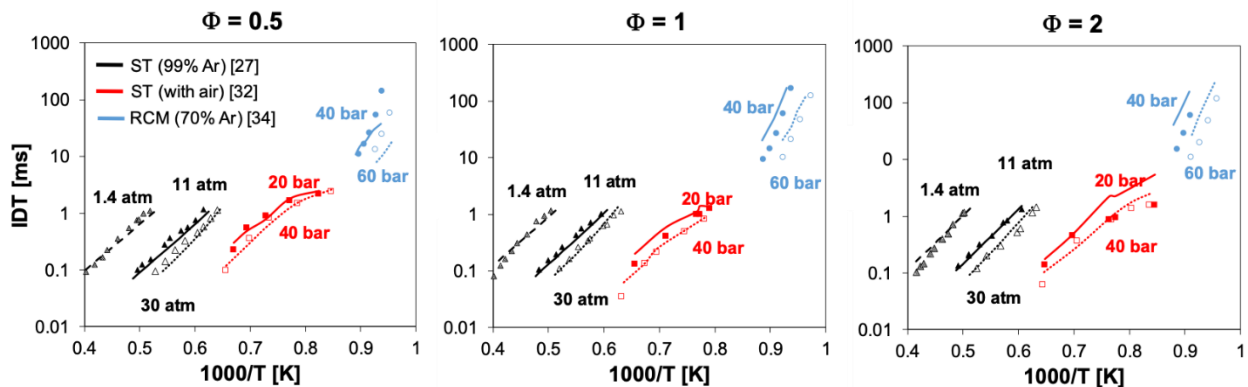


Figure 14 - Ignition delay times at low, intermediate and high temperature at variable  $\Phi$  and  $P_c$ : experimental and modeling results.

In order to understand the deviations under the richest conditions, a sensitivity analysis for OH mole fraction was performed under 3 representative conditions of the respective experimental campaigns at similar (high) pressures, at the beginning of the ignition phenomenon ( $\sim 1\%$   $\text{NH}_3$  conversion). Figure 15 shows the related results: at low and intermediate temperatures, the key role of  $\text{H}_2\text{NO}$  is confirmed again, and the reactions promoting its formation (R15 and R18) and H-abstraction via  $\text{O}_2$  (R36) drive the reactivity of the system. On the other side, the competition between branching and termination in the  $\text{NH}_2 + \text{NO}$  path (R16 and R17) has a primary role. On this regard, it is worth mentioning that the adopted rates for this path are pressure-independent. Recently, Klippenstein<sup>24</sup> reported a possible stabilization of reaction intermediates at higher pressures, resulting in an increase of the selectivity of the branching route R17. Therefore, considering such dependence could then improve the agreement with the data of He et al.,<sup>34</sup> although currently no pressure-dependent rates are available.

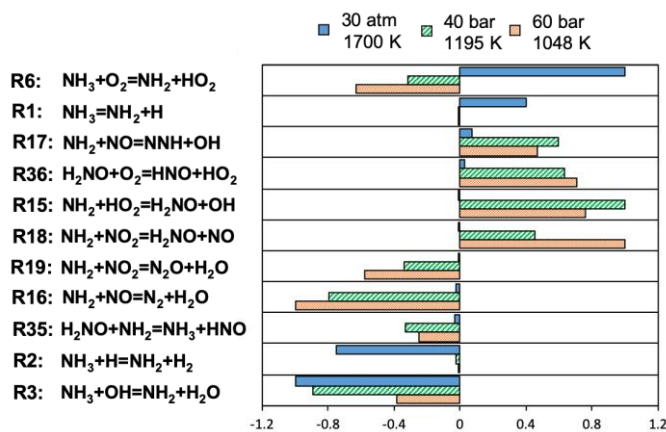


Figure 15 - Sensitivity coefficients to OH mole fraction at  $\Phi = 2$ , normalized with respect to the local maximum value, in correspondence of 1% ammonia conversion. The reaction  $\text{H} + \text{O}_2 = \text{O} + \text{OH}$  is omitted.

Finally, at higher temperatures, the H-abstraction on NH<sub>3</sub> by O<sub>2</sub> (R6) has an opposite effect with respect to low- and intermediate- temperature, and drives reactivity together with ammonia decomposition (R1), whilst H-abstractions by H and OH slow down the system, since subtracting active radicals from the related pool. In this case, the best agreement is found with the experiments.

### 3.2.4. Laminar flame speed

The prediction of laminar flame speed of ammonia flames is particularly critical because of the very low speed values compared to conventional hydrocarbons. This makes experimental campaigns more challenging, since with such low rates the relative weight of buoyancy forces is no longer negligible. Hayakawa et al.<sup>85</sup> showed that, when experimentally investigating spherically propagating flames of NH<sub>3</sub>/air, buoyancy caused the movement of the flame center and the loss of the spherical assumption. This can affect the usability of such data for the validation of kinetic models, which is usually carried out by using 1D solvers. Therefore, in this work the capability of the developed mechanism in predicting laminar flame speed is verified by using the experimental data collected by Ronney<sup>81</sup> under microgravity conditions. For the sake of completeness, recent results obtained by Mei et al.<sup>83</sup> under gravity conditions, but in a more limited range of equivalence ratios are added. Moreover, Nakamura and Shindo<sup>86</sup> recently showed that, differently from methane flames, the effects of radiation heat loss on NH<sub>3</sub> flame speeds at ambient  $T$  and  $P$  were significant in a wide range of  $\Phi$ , with a particular emphasis on lean and rich conditions. Therefore, radiation effects were accounted for through an optically-thin model.<sup>87</sup> Results are shown in Figure 16, and highlight a very good agreement of the model at lean, stoichiometric and slightly rich conditions, with a small overestimation (less than 1 cm s<sup>-1</sup>) for  $\Phi$  close to the rich extinction ( $\sim 1.7$ ).

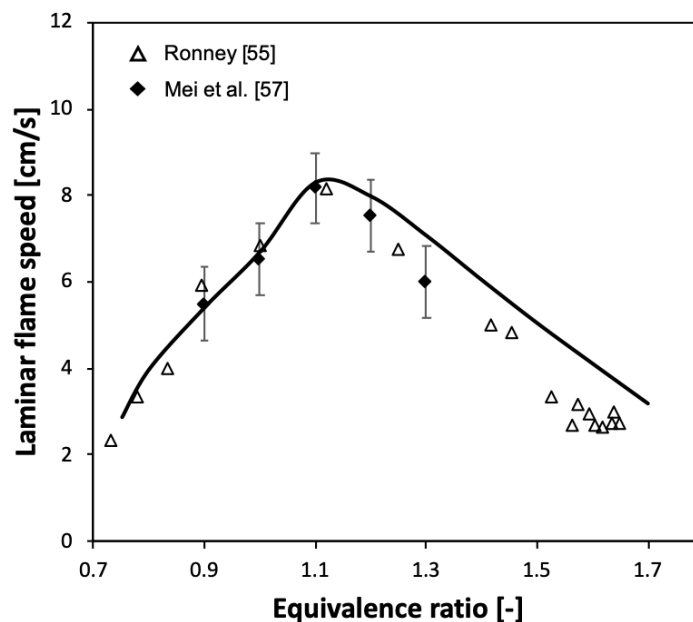


Figure 16 - Laminar flame speed of NH<sub>3</sub>/air mixtures at  $P = 1$  atm,  $T = 298$  K.

A deeper insight within the obtained results was obtained via sensitivity analysis to the flame speed (Figure 17) for lean, stoichiometric and rich compositions, respectively. In all of them, it can be noticed that the competition between branching and termination of the  $\text{NH}_2 + \text{NO}$  reaction is again crucial (R16 and R17), but above all the production of H radicals via  $\text{NH}_2 + \text{NH}$  (R7) is the most enhancing path. HNO dissociation, which was studied in this work (R28), is also an important step under lean and stoichiometric conditions. Anyway, the most peculiar result is the inhibiting effect of R23, in spite of its production of H radicals. This can be attributed to the removal of  $\text{NH}_2$  radicals from the just mentioned branching path R17 as well as R7. In addition, such path removes O radicals from the usual branching paths of the core  $\text{H}_2/\text{O}_2$  mechanism. A more accurate estimation of R23 is then a critical milestone of the ammonia mechanism, and to the authors knowledge, the only temperature-dependent theoretical estimations of such constant were obtained by Bozzelli and Dean<sup>88</sup> and Sumathi et al.<sup>60</sup> (used in this work), differing from each other by a factor of  $\sim 1.4$  at 1000–2000 K. R23 also had a boosting effect on the production of NO at intermediate and high-temperatures in flow reactor (Figures 11 and 13), as already pointed out by Glarborg et al. in their review.<sup>31</sup> Therefore, considering the role of R23 within the current mechanism, the accuracy of those two datasets is somehow competitive.

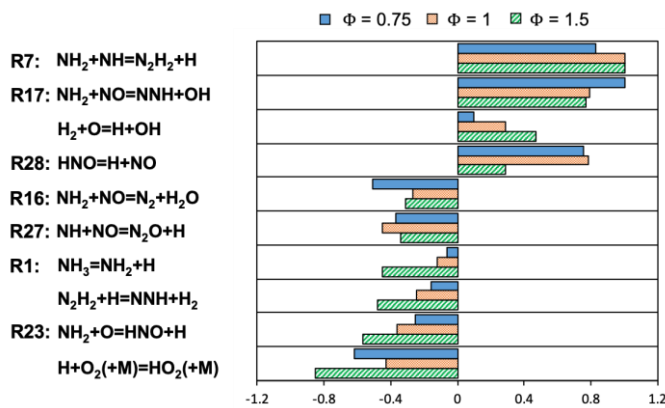


Figure 17 - Sensitivity coefficients (normalized with respect to the maximum value) to laminar flame speed at  $T = 298$  K and  $P = 1$  atm for different  $\Phi$ . The reaction  $\text{H} + \text{O}_2 = \text{O} + \text{OH}$  is not reported.

A more complete validation of the kinetic mechanism in terms of laminar flame speed predictions, with different oxidizer compositions can be found in the Supplementary Material.

#### 4. Conclusions

The renewed interest raised by  $\text{NH}_3$  combustion in the recent years has made available a significant amount of experimental data, characterizing its reactivity in a wide range of operating conditions. Yet, a comprehensive understanding of its kinetic behavior is still an open challenge, especially at low-temperature ( $T < 1200$  K) and under diluted conditions, on which the combustion community is devoting a significant effort because of the potentially lower  $\text{NO}_x$  emissions. In this work, this topic was addressed through a combined experimental and theoretical approach, able to shed light on the



kinetic behavior of ammonia affecting low-temperature, diluted conditions. New experimental data were collected in jet-stirred and flow reactors at pressure close to atmospheric, in such a way to cover the whole range of temperatures (500–2000 K). In order to interpret these results, a theoretical analysis was performed to evaluate some of the most critical steps in the pyrolysis and oxidation mechanisms. By means of sensitivity analysis and literature review, the most critical reaction steps, not yet systematically investigated either experimentally or theoretically, were identified. Thus, the rate constants for ammonia decomposition, H-abstractions and the dissociation of the HNO intermediate were evaluated and included in a comprehensive kinetic model, built up following a first-principles approach, and incorporating the state-of-the-art kinetic rates.

The kinetic analysis of the low-temperature experiments allowed the identification of a peculiar behavior. Up to  $\sim 1200$  K, the high amount of HO<sub>2</sub> radicals present in the system results in the inversion of the initiation via O<sub>2</sub>, i.e.  $\text{NH}_3 + \text{O}_2 = \text{NH}_2 + \text{HO}_2$  (recalculated in this work) acting instead as a termination step. Therefore, the reactivity of the systems is shifted to higher temperatures, and is distributed in a wider temperature range with increasing O<sub>2</sub> concentration. The key role of H<sub>2</sub>NO was highlighted, as already reported in the literature, and the related H-abstractions by O<sub>2</sub>, HO<sub>2</sub>, NH<sub>2</sub> and NO<sub>2</sub> were found to affect reactivity at the lowest temperatures.

The comprehensiveness of the kinetic mechanism was also verified in the prediction of ignition delay time and flame propagation, where the key role of the newly-introduced kinetic rates was confirmed. At higher pressures and low temperatures, H<sub>2</sub>NO was found to play a pivotal role in controlling ignition delay time. In this regard, theoretical work for the estimation of the H-abstractions on H<sub>2</sub>NO and the effect of pressure on NH<sub>2</sub> + NO selectivity could further improve the predictability of the kinetic model in such conditions. Lastly, the prediction of laminar flame speeds highlighted the key, decelerating effect of the reaction  $\text{NH}_2 + \text{O} = \text{HNO} + \text{H}$ , which promotes instead NO formation at high temperature, as found out in the analysis of flow reactor experiments. Further theoretical study on it can be useful for a more accurate, temperature-dependent re-evaluation of this step.

## Nomenclature

### Roman symbols

$P$	Pressure [Pa]
$T$	Temperature [K]

### Greek symbols

$\tau$	Residence time [s]
$\Phi$	Equivalence ratio [-]

### Acronyms

BSF	Burner-stabilized flame
DFT	Density functional theory
FR	Flow reactor

IDT	Ignition delay time
JSR	Jet-stirred reactor
LFS	Laminar flame speed
ME	Master equation
NO <sub>x</sub>	Nitrogen oxides
PES	Potential energy surface
ppm	Parts per million
PW	Present work
RCM	Rapid compression machine
ST	Shock tube
VTST	Variational transition state theory

#### Subscripts

c	After compression
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