HAL
open science

ON AMMONIA KINETICS OF OXIDATION UNDER HIGHLY TURBULENT CONDITIONS AND IMPACT OF NITRIC OXIDE

Philippe Dagaut

▶ **To cite this version:**

Philippe Dagaut. ON AMMONIA KINETICS OF OXIDATION UNDER HIGHLY TURBULENT CONDITIONS AND IMPACT OF NITRIC OXIDE. 2nd Symposium on Ammonia Energy, University of Orléans, Jul 2023, ORLEANS, France. hal-04165877

HAL Id: hal-04165877

https://univ-orleans.hal.science/hal-04165877v1

Submitted on 19 Jul 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Public Domain

THE JOURNAL OF Ammonia Energy

Cardiff University Press | Gwasg Prifysgol Caerdydd

2nd Symposium on Ammonia Energy

ON AMMONIA KINETICS OF OXIDATION UNDER HIGHLY TURBULENT CONDITIONS AND IMPACT OF NITRIC OXIDE

Dagaut, Philippe[a*]

[a]*CNRS 1C Avenue de la Recherche Scientifique, Orléans, France*

* Corresponding author.
e-mail address: philippe.dagaut@cnrs-orleans.fr

Topics: Combustion Fundamental, Reaction Modelling

Introduction

Ammonia has been used extensively for the selective non-catalytic reduction (SNCR) of nitric oxide (NO). This process efficiently reduces NO over a limited temperature range centred around 1200 to 1250 K. Experimental and kinetic modelling studies of SNCR are numerous[1-5].

Nowadays, the interest for ammonia as energy carrier or fuel is rising. Indeed, ammonia is regarded as a zero-carbon alternative fuel usable in power stations[6] including gas turbines [7]. However, its combustion needs further studies [6] and kinetic interpretation of experimental results needs further investigations since it has been reported that kinetic reaction mechanisms have weaknesses and occasionally fail to simulate the kinetics of oxidation of ammonia [6]. Furthermore, under practical conditions, turbulence and recirculation favour the interaction between ammonia and nitrogen oxides and may influence ammonia overall kinetics of oxidation.

We report experimental results obtained in a jet-stirred reactor (JSR) at 1 bar for several equivalence ratios in the range 0.1 to 2, for several initial mole fractions of ammonia and nitric oxide, at fixed mean residence times and over a range of temperature. Kinetic modelling of JSR experiments and burning velocities was performed and reaction pathway analyses were performed to interpret the results.

Materials and Methods

Oxidation experiments were completed using a small volume (27.5 cm^3) fused-silica JSR introduced previously [8]. It consists of a 40 mm o.d. sphere equipped with 4 injectors (nozzles of 1 mm i.d.), for the admission of the gases which achieve the stirring. The JSR is located inside a temperature-controlled electric oven (1500 W), isolated by ceramic wood. In the experiments, high dilution by nitrogen was used. Ammonia, nitric oxide, N_2, and O_2 flows were delivered using thermal mass-flow meters. The JSR operated under macro-mixing conditions which allows using of a perfectly-stirred reactor model. A good thermal homogeneity along the vertical axis of the reactor was observed in the experiments using a Pt/Pt-Rh10% thermocouple of 0.1 mm diameter located inside a thin-wall fused-silica tube (<0.5mm), which avoids catalytic reactions on the thermocouple wires. Thanks to a high degree of dilution the temperature rise in the JSR was small (<20 K). Samples of the reacting mixtures (30–40 Torr) were collected via a sonic quartz probe for off-line gas chromatography (GC) analyses. To increase the detection of samples components by GC, they were pressurized at 1 bar before injection into the GC column, using an in-house glass piston. Quantification of permanent gases was done using a GC with thermal conductivity detector. The mole fractions of H_2O, NO, NO_2, N_2O, and NH_3 were measured on-line by Fourier transform infrared spectroscopy (FTIR). The uncertainties on mole fractions were determine to be in the range ±10to 15% for the reactants and products.

Kinetic modelling was performed using the PSR software [9]. Flame speeds modelling was carried out using the PREMIX computer code [10]. Several published kinetic model were used: a SNCR-SOx scheme [4], a HCN-NOx model named DGA mechanism [11], Konnov mechanism [12], and the kinetic reaction mechanisms of Song et al. [13], and Otomo et al. [14].

Results and Discussions

Experiments were completed at 1 bar for the equivalence ratios φ equal to 0.1, 0.5, 1, and 2. Here, we define $\varphi = (NH_3\% / O_2\%) / (NH_3\% / O_2\%)_{at\ \varphi=1}$ and ammonia global oxidation by $NH_3 + 1.25\ O_2 = NO + 1.5\ H_2O$. We considered two initial mole fractions of ammonia (500 and 1000 ppm) and three initial mole fractions of nitric oxide (0, 500, and 1000 ppm). The experiments were carried out at two residence times, i.e., τ = 0.1 and 0.2 s. The JSR temperature was increased stepwise from 1100 to 1450 K. The mole fractions of the reactants O_2, NH_3, and NO, and of the products NO, NO_2, N_2O, and H_2O were obtained.
Our experimental results showed a significant effect of nitric oxide on ammonia conversion, not described in the literature. Indeed, the presence of 500–1000 ppm of nitric oxide reduces fuel-lean and fuel-rich NH_3 ignition temperature by ~120 K.

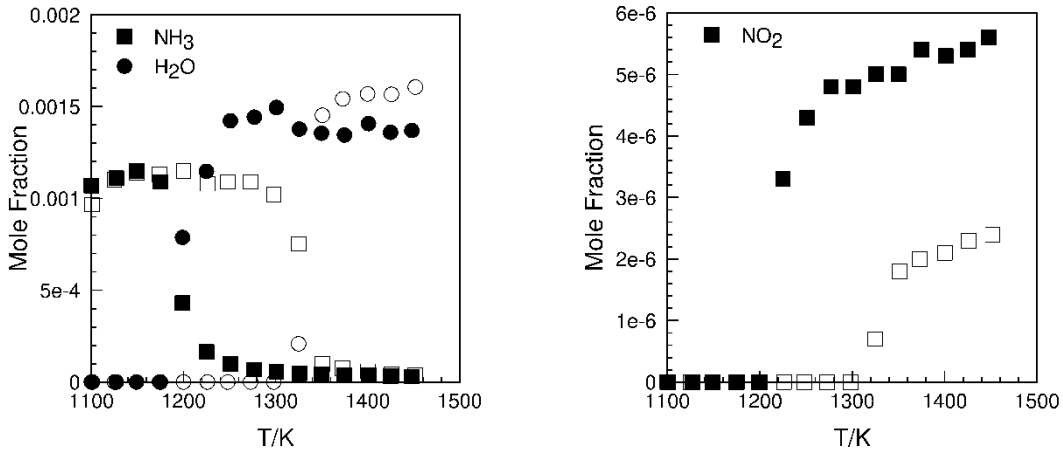

Figure 1. Impact of nitric oxide on ammonia conversion in a jet-stirred reactor at 1 bar: 0.1% NH_3, 1.25% of O_2, τ=100 ms; φ=0.1; no NO (open symbols), 1000 ppm of NO (solid symbols).

At the same time, the conversion of NO to NO_2 was favoured by the presence of ammonia.
Several published kinetic reaction schemes were used to model our JSR experiments. We observed that the fastest simulated oxidation of NH_3 was obtained by the scheme of Konnov [12], which is in line with results of previous modelling efforts [6, 15]. The schemes of Song et al. [13] and Otomo et al. [14] also overestimates the rate of oxidation of. We also tested the previously proposed DGA model [11] because it was reported by Kobayashi et al. [6] that it could predict well ammonia ignition in a shock-tube [16] and ammonia burning velocities. Indeed, we found that the DGA scheme performs better than the other kinetic schemes tested here. Nevertheless, the DGA scheme slightly over predicts ammonia-air burning velocities. Hence, sensitivity analyses were conducted to identify possible ways of improving the predictions of ammonia-air burning velocities and keeping good predictions of JSR data. It was found that the kinetics of $NH_2 + H \rightleftharpoons NH + H_2$ and $HNO + H \rightleftharpoons NO + H_2$ were significantly influencing the simulation results for flame speeds but not those of JSR or shock-tube. We updated the DGA scheme using the kinetic parameters proposed by Otomo et al. [14] for these two reactions. The updated kinetic reaction scheme could well predict flame speeds, JSR and shock tube data. Sensitivity analyses were also carried out to identify the reactions influencing the most predictions of published reaction mechanisms and rationalise discrepancies observed between simulations and JSR data.

Conclusions

Experiments performed in a JSR under turbulent conditions at 1 bar for several equivalence ratios (0.1 to 2), initial mole fractions of ammonia (500 to 1000 ppm) and NO (0 to 1000 ppm) revealed significant acceleration of ammonia ignition and oxidation by nitric oxide and conversion of NO to NO_2.
A previously proposed kinetic model [11] was updated to improve the modelling of ammonia-air flame speeds. It could be used to well predict the JSR data, ammonia ignition, and ammonia-air flame speeds. According to computation using that updated model, the mutual sensitization of the oxidation of NH_3 and NO is due to a sequence of reactions producing (i) OH and (ii) HO_2 radicals, principally involved in the oxidation of ammonia: (i) $NH_2 + NO \rightarrow NNH + OH$, $NNH \rightarrow N_2 + H$, $H + O_2 \rightarrow OH + O$, and (ii) $NNH + O_2 \rightarrow N_2 + HO_2$ and $H + O_2 + M \rightarrow HO_2 + M$, $NO + HO_2 \rightarrow NO_2 + OH$.

Acknowledgements

Support from the CAPRYSSES project (ANR- 11-LABX-006–01) funded by ANR through the PIA (Programme d'Investissement d'Avenir) is gratefully acknowledged.

References

1. Miller, J.A. , C.T. Bowman, Mechanism and modeling of nitrogen chemistry in combustion. *Progress in Energy and Combustion Science*, **1989**, *15*, 287-338.
2. Miller, J.A. , P. Glarborg, Modeling the Thermal DeNOx Process: Closing in on a Final Solution. *Int. J. Chem. Kinet.*, **1999**, *31*, 757-765.
3. Schmidt, C.C. , C.T. Bowman, Flow reactor study of the effect of pressure on the thermal De-NOx process. *Combustion and Flame*, **2001**, *127*, 1958-1970.
4. Dagaut, P. , A. Nicolle, Experimental and kinetic modeling study of the effect of SO2 on the reduction of NO by ammonia. *Proceedings of the Combustion Institute*, **2005**, *30*, 1211-1218.
5. Javed, M.T., Z. Ahmed, M.A. Ibrahim, N. Irfan, A comparative kinetic study of SNCR process using ammonia. *Brazilian Journal of Chemical Engineering*, **2008**, *25*, 109-117.
6. Kobayashi, H., A. Hayakawa, K.D.Kunkuma A. Somarathne, Ekenechukwu C. Okafor, Science and technology of ammonia combustion. *Proceedings of the Combustion Institute*, **2019**, *37*, 109-133.
7. Kurata, O., N. Iki, T. Matsunuma, T. Inoue, T. Tsujimura, H. Furutani, H. Kobayashi, A. Hayakawa, Performances and emission characteristics of NH3–air and NH3CH4–air combustion gas-turbine power generations. *Proceedings of the Combustion Institute*, **2017**, *36*, 3351-3359.
8. Dagaut, P., M. Cathonnet, J.P. Rouan, R. Foulatier, A. Quilgars, J.C. Boettner, F. Gaillard, H. James, A jet-stirred reactor for kinetic studies of homogeneous gas-phase reactions at pressures up to ten atmospheres (≈1 MPa). *Journal of Physics E: Scientific Instruments*, **1986**, *19*, 207-209.
9. Glarborg, P., R.J. Kee, J.F. Grcar, J.A. Miller, *PSR: A FORTRAN program for modeling well-stirred reactors.*, in *SAND86-8209*. 1986, Sandia National Laboratories: Livermore, CA.
10. Kee, R.J., J.F. Grcar, M.D. Smooke, J.A. Miller, *A Fortran program for modeling steady laminar one-dimensional premixed flames.*, in *SAND85-8240*. 1985, Sandia National Laboratories: Livermore, CA.
11. Dagaut, P., P. Glarborg, M.U. Alzueta, The oxidation of hydrogen cyanide and related chemistry. *Progress in Energy and Combustion Science*, **2008**, *34*, 1-46.
12. Konnov, A.A., Implementation of the NCN pathway of prompt-NO formation in the detailed reaction mechanism. *Combustion and Flame*, **2009**, *156*, 2093-2105.
13. Song, Y., H. Hashemi, J.M. Christensen, C. Zou, P. Marshall, P. Glarborg, Ammonia oxidation at high pressure and intermediate temperatures. *Fuel*, **2016**, *181*, 358-365.
14. Otomo, J., M. Koshi, T. Mitsumori, H. Iwasaki, K. Yamada, Chemical kinetic modeling of ammonia oxidation with improved reaction mechanism for ammonia/air and ammonia/hydrogen/air combustion. *International Journal of Hydrogen Energy*, **2018**, *43*, 3004-3014.
15. Nakamura, H. , S. Hasegawa, Combustion and ignition characteristics of ammonia/air mixtures in a micro flow reactor with a controlled temperature profile. *Proceedings of the Combustion Institute*, **2017**, *36*, 4217-4226.
16. Mathieu, O. , E.L. Petersen, Experimental and modeling study on the high-temperature oxidation of Ammonia and related NOx chemistry. *Combustion and Flame*, **2015**, *162*, 554-570.