Reaction kinetics of nitrogen compounds in combustion systems

Final report of NKFIH OTKA Grant K116117

The research activity supported by this OTKA grant can be divided to the following topics:

1) Development of methods and software tools for the analysis of detailed reaction mechanisms.
2) Comparison of the accuracy of widely used NOx reaction mechanisms on selected sets of nitrogen-chemistry experimental data
3) Determination of the rate coefficients of several important elementary reactions of high-temperature nitrogen chemistry

1) Development of methods and software tools for the analysis of detailed reaction mechanisms

Complex kinetic reaction schemes are widely used in many areas of science and technology for computer simulations, but numerical analysis of these schemes may provide further insight. Pathway analysis identifies the key chemical transformations. Sensitivity analysis shows which are the most important parameters, and uncertainty analysis may be used for the assessment of the confidence that can be placed in simulation results. Mechanism reduction methods can produce reduced schemes that provide almost identical simulation results using much less computer time, thus allowing engineering optimizations. These topics were reviewed in an article [1] published in a "Reference Module in Chemistry, Molecular Sciences and Chemical Engineering" by Elsevier.

Applications of global sensitivity and uncertainty methods for models with correlated parameters are essential to investigate chemical kinetics models. A new global sensitivity analysis method was elaborated that is able to handle correlated parameter sets. It is based on the coupling of the Rosenblatt transformation with an optimized Random Sampling High Dimensional Model Representation method. The accuracy of the computational method was tested on a series of examples where the analytical solution was available. The capabilities of the method were also investigated by exploring the effect of the uncertainty of rate parameters of a syngas–air combustion mechanism on the calculated ignition delay times. Most of the parameters have large correlated sensitivity indices and the correlation between the parameters has a high influence on the results. It was demonstrated that the values of the calculated total correlated and final marginal sensitivity indices are independent of the order of the decorrelation steps. The final marginal sensitivity indices are meaningful for the investigation of the chemical significance of the reaction steps. The parameters belonging to five elementary reactions only, have significant final marginal sensitivity indices. Local sensitivity indices for correlated parameters were defined which are the linear equivalents of the global ones. The results of the global sensitivity analysis were compared with the corresponding results of local sensitivity analysis. The same set of reactions was indicated to be important by both approaches. The results were published in [2].

Accurate calculation of the concentrations of hydrocarbon radicals is crucial for the investigation of NOx production and removal in combustion systems. A possible approach to create skeletal models is to start from a reliable detailed mechanism and then keeping only the significant terms in the rate expressions and applying the QSSA and partial equilibrium approximations. In our work [3], the low temperature first ignition of *n*-butane/air mixtures was studied, using a short chemistry model with all the important isomers. The reaction rate coefficients were obtained from the mechanism of Healy *et al.* (*Combust. Flame*, **157**, 1526-1539 (2010)). The first ignition delay time and the overall heat release (temperature jump) were obtained analytically in closed form, where the parametric influence can be easily seen.

During the years of the grant, there was a continuous development of the methodology for the collection and interpretation of combustion experimental data, storage of the data in XML-format files, and development of software tools for the comparison of reaction mechanisms and optimization of reaction mechanisms. The latter means the determination of rate parameters of elementary reactions via fitting to experimental data withing the physically realistic domain of the parameters. This domain is established by the direct measurements of the rate coefficients or theoretical calculations.

The collected experimental data were always stored in a format called Respecth Kinetics Data Format (RKD-format) and published in the ReSpecTh Information System [4]. The RKD-format is defined in document [5]. Optima++ [6] is a C++ language framework code for the creation of RKD-format files, making comparison of detailed reaction mechanisms using the RKD-format datafiles and optimization of reaction mechanisms. In the last five years, there was a significant development work on the RKD-format and the Optima++ code; new versions were published in every year. The motivation of the development was always to answer the new requirements of the current research topics. The development of RKD-format and the Optima++ code was documented in the ReSpecth Information System. In the journal publications, we always referred to the latest versions of the RKD-format and the Optima++ code. Our work on the RKD-format and the Optima++ code was disseminated in a series of Youtube videos [7].

2) Comparison of the accuracy of widely used NOx reaction mechanisms on selected set of nitrogen-chemistry experimental data

Isocyanic acid (HNCO) is a primary decomposition product of both cyanuric acid (HOCN) and urea (H_2NCONH_2) in combustion systems. It plays an important role in the selective non catalytic reduction (SNCR) of nitrogen-oxides. Experimental articles dealing with the oxidation and pyrolysis of isocyanic acid were evaluated. XML files using the ReSpecTh RKD 2.0 format were created from the data series of these measurements. Based on these data, 6 detailed reaction mechanisms were investigated. None of the examined mechanisms could well reproduce the measurements of Glarborg and his co-workers (*Combustion and Flame*, **98**, 241-258(1994)). The Arrhenius parameters of the important elementary reactions published in this Glarborg et al. article were very different from those of the same reactions in the contemporary mechanisms. For the rest of the experimental data, the two best mechanisms were the Glarborg-2018 and the POLIMI-2018 reaction mechanisms. The most important elementary reactions at the various conditions were identified using local sensitivity analysis. The lists of the important

reactions according to the two examined mechanisms were in agreement, but the order of importance was different. Two elementary reactions were sensitive at most of the examined data points. These were elementary reactions HNCO+M=CO+NH+M and HNCO+NH=NH_2+NCO. Preliminary results have been published in the BSc Thesis [8] of Bence Horváth.

Several experimental papers have dealt with the NOx formation during syngas combustion Large amount of experimental data were extracted from these papers and encoded to RKD-format XML files. The performance of three recently published combustion mechanisms that can describe the combustion syngas/NOx gas mixtures were investigated against these experimental data. The Zhang-2017 and Glarborg-2018 mechanisms provided somewhat better results than the POLIMI-2019 mechanism. Two mechanistic details were also investigated. In future syngas combustion mechanisms, the HOCO chemistry should be included since it has a significant effect in high-pressure ($p > 20$ bar) experiments. In terms of the $N_2O + H_2 = N_2 + H_2O$ reaction, the disagreement between two recent direct measurements was investigated and it was found that in the future, the rate coefficient measured by Mulvihill et al. (2018) should be used for the reaction instead of that measured by Kosarev et al. (2007). Preliminary results have been published in the OTDK student report [9] and BSc Thesis [10] of András Szanthoffer and in the conference article [11] of Szanthoffer et al. We are currently working on a revised and extended journal publication. OTDK is the acronym of Hungarian Scientific Students' Associations Nationwide Conference.

The experimental data of Song *et al.* (*Proc. Combust. Inst.*, **37**, 667–675 (2018)) on the oxidation of methane accelerated by nitric oxide were reproduced by computer simulations using three different detailed NOx combustion reaction mechanisms. The three mechanisms studied were: POLIMI-2019 (156 species / 2262 reaction steps), Glarborg-2018 (153/1450) and Shrestha-2019 (129/1196). The Glarborg mechanism proved to be the most accurate. The importance of the reaction steps was investigated by local sensitivity analysis at the conditions of the experiment. A preliminary version of the results has appeared in the in the OTDK student report [12] and BSc Thesis [13] of Henrik Schuszter.

Reburning is a widely used industrial approach for the conversion of NO to N_2 by methane and ethane in high temperature gas mixtures. Conversions of nitric oxide in the presence of methane and ethane was investigated using the concentration profile measurements carried out in a flow reactor by Alzueta et al. (*Combust. Flame*, **109**, 25–36 (1997)). Kinetic simulations for the reproduction of these experimental data were carried out with program Optima++ and the OpenSmoke++ solver package. The simulations were performed using four nitrogen chemistry mechanisms: POLIMI-2019, Glarborg-2018, GRI 3.0-1999 and Shrestha-2019. Based on the comparison of the error function values, POLIMI-2019 seems to be the best mechanism, but simulations with Shrestha-2019 reproduced the experimental data similarly well. Glarborg-2018 gave good results at low temperatures only. Local sensitivity analysis was used for the determination of the most important reactions at the various experimental conditions. A preliminary version of the results has appeared in the OTDK student report [14] and BSc Thesis [15] of Ákos Veres-Ravai, and we are working on a related journal publication.

Ammonia is a potential fuel for the storage of thermal energy. Also, experimental data on ammonia combustion may be used for testing the $NH_3/NH_2/NH$ transformation pathways present in the NO formation routes of the combustion of hydrocarbons. Experimental data were collected for homogeneous ammonia combustion: ignition delay times measured in shock tubes (247 data points in 28 datasets from four publications) and species concentration measurements from flow reactors (194/22/4). The measurements cover wide ranges of temperature T, pressure p, equivalence ratio φ and dilution. The experimental data were encoded in ReSpecTh Kinetics Data Format version 2.2 XML files. The standard deviations of the experimental datasets used were determined based on the experimental errors reported in the publications and also on error estimations obtained using program MinimalSplineFit. Simulations were carried out with eight recently published mechanisms (Mével-2009, Klippenstein-2011, Abian-2015, Zhang-2017, Glarborg-2018, Shrestha-2018, POLIMI-2019, Kovács-2020) at the conditions of these experiments using the Optima++ framework code, and the FlameMaster and OpenSmoke++ solver packages. The performance of the mechanisms was compared using a sum-of-square error function to quantify the agreement between the simulations and the experimental data. Ignition delay times were well reproduced by five mechanisms, the best ones were Glarborg-2018 and Shrestha-2018. None of the mechanisms were able to reproduce well the profiles of NO, N_2O and NH_3 concentrations measured in flow reactors. The results were published in the MSc Thesis of Gergely Juhász [16] and in a journal article [17].

3) Determination of the rate coefficients of several important elementary reactions of high-temperature nitrogen chemistry

A re-evaluation of the flow reactor experiments of Abián *et al.* (Abián, M.; Alzueta, M. U.; Glarborg, P. Formation of NO from N_2/O_2 Mixtures in a Flow Reactor: Toward an Accurate Prediction of Thermal NO. *Int. J. Chem. Kinet.*, **47**, 518−532 (2015); DOI: 10.1002/kin.20929) was carried out. In these experiments, nitrogen oxide formation was measured at atmospheric pressure in the temperature range of 1700–1810 K using several mixtures containing different ratios of oxygen, nitrogen, and water vapor. At such conditions nitric oxide is mainly produced via the so-called thermal route. Based on the mechanism of Abián et al., the two most important reaction steps for NO formation ($NO + N = N_2 + O$ and $N_2O + O = 2\ NO$) were identified by local sensitivity analysis. For the optimization of the Arrhenius parameters of these reaction steps, 25 data points measured by Abián *et al.*, two direct rate coefficient measurements (73 data points), and one theoretical calculation were used.

R1 $NO + N = N_2 + O$ A = 1.176E+10 $cm^3\ mol^{-1}\ s^{-1}$, n = 0.935, E/R = -693.68 K
R2 $N_2O + O = 2\ NO$ A = 1.748E+16 $cm^3\ mol^{-1}\ s^{-1}$, n = -0.557, E/R = 14 447 K

The obtained mechanism with the optimized Arrhenius parameters described the results of the flow reactor experiments, direct measurements, and theoretical calculations much better compared to the Abián et al. mechanism and also the widely used GRI-Mech 3.0 and Konnov-2009 NO_x mechanisms. The rate coefficients of these elementary reactions were obtained with low uncertainty in the temperature range of 1600–2200 K. These results were published in the BSc thesis [18] of Noémi Anna Buczkó and in a journal publication [19].

The experiments of Rahinov *et al.* (*Combust. Flame*, **145**, 105-116 (2006)) measuring NH_2 concentration profiles in methane–air laminar flat flames doped with ammonia were re-evaluated. The flames were simulated with the FlameMaster code using a modified POLIMI combustion mechanism. Based on local sensitivity analysis results, Arrhenius parameters A, n, E of reaction steps $NH_2 + H = NH + H_2$ and $NH_3 + OH = NH_2 + H_2O$ were selected for optimization, which took into account not only the experimental data of Rahinov *et al.*, but also related direct measurements and theoretical determinations as optimization targets.

R3	$NH_2+H=NH+H_2$	$A = 2.129 \times 10^{21}$ cm^3 mol^{-1} s^{-1}, n = -2.25, E/R = 4150 K
R4	$NH_3+OH=NH_2+H_2O$	$A = 4.500 \times 10^{10}$ cm^3 mol^{-1} s^{-1}, n =0.560, E/R = 730 K

The optimized mechanism described the measured concentration profiles better than the original one, while the new rate parameter values were within the prior uncertainty limits obtained from the evaluation of literature data. The optimization process also provided new posterior uncertainty limits, which are within the prior uncertainty limits. The results were published in journal article [20].

Literature experimental data were collected about hydrogen–oxygen combustion systems doped with NO, NO_2 or N_2O, also about H_2/N_2O combustion systems. The data included concentration measurements in jet stirred reactors, ignition delay time measurements in shock tubes, concentration measurements in tubular flow reactors, laminar burning velocity measurements and concentration profile measurements in burner stabilized flames. In total, 4949 data points in 207 data sets from 35 publications were used. These experimental data were reproduced using sixteen NOx mechanisms. The performance of the Nakamura-2017, Glarborg-2018 and Zhang-2017 mechanisms were the best. Nine elementary reactions were selected from the Glarborg-2018 mechanism based on sensitivity analysis and the Arrhenius parameters (A, n, E) of these reactions were fitted not only to selected indirect experimental data (1285 data points in 52 data sets), but also direct experimental and theoretical determinations of the rate coefficients (705 data points in 48 data sets).

The following new rate parameters were determined:

R5	$NO_2 + H = NO + OH$	A = 1.574E+14 cm^3 mol^{-1} s^{-1}, n = 0, E/R = 144.84 K
R6 LP	$N_2O + M = N_2 + O + M$	A = 1.810E+29 cm^3 mol^{-1} s^{-1}, n = –3.962, E/R = 34809 K
R7	$N_2O + H = N_2 + OH$	A = 1.577E+02 cm^3 mol^{-1} s^{-1}, n = 3.278, E/R = 3096.6 K
R8	$NO + HO_2 = NO_2 + OH$	A = 4.553E+13 cm^3 mol^{-1} s^{-1}, n =–0.433, E/R = –94.969 K
R9 LP	$NO + H + M = HNO + M$	A = 7.950E+21 cm^6 mol^{-2} s^{-1}, n =–2.093, E/R = 492.17 K
R10	$NH + NO = N_2O + H$	A = 2.713E+14 cm^3 mol^{-1} s^{-1}, n =–0.575, E/R = –359.92 K
R11	$NH + OH = HNO + H$	A = 4.951E+11 cm^3 mol^{-1} s^{-1}, n = 0.476, E/R = –452.80 K
R12	$HNO + H = NO + H_2$	A = 2.817E+16 cm^3 mol^{-1} s^{-1}, n = –0.938, E/R = 1332.6 K
R13 LP	NO+OH+M=HONO+M	A = 5.582E+24 cm^6 mol^{-2} s^{-1}, n = –2.974, E/R = 47.473 K

(LP stands for low-pressure limit)

This way more accurate rate parameters of these reactions could be obtained, and the temperature dependent uncertainty of the rate coefficients was calculated. The Glarborg-2018 mechanism modified with the optimized rate parameters described the experimental data better than any other investigated reaction mechanism.

This project evolved during the years, and became more and more comprehensive. First, only experiments carried out in shock tubes and flow reactors were investigated and 7 published mechanisms were compared using these data. The results were published in the year 2016 OTDK report of Márton Kovács [21]. In the next stage, the number of investigated mechanisms was increased to 16, and the scope of experimental data was extended to perfectly stirred reactors, laminar burning velocities and species profiles measured in flat flames. Also, the collected data were used for the determination of the rate parameters of 9 elementary reactions. These results were discussed in the year 2018 OTDK report of Márton Kovács [22]. For this work, he received the 1st Prize in Division Reaction Kinetics and Catalysis I., Section Chemistry and Chemical Engineering of OTDK, therefore the same work was accepted as an MSc Thesis [23]. The results were published first in a conference paper [24] and then in a journal article [25].

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Tamás Turányi, PI