



Testing of Kinetic Mechanisms Using a Large Amount of Experimental Data on NH_3/H_2 and $\text{NH}_3/\text{syngas}$ Combustion

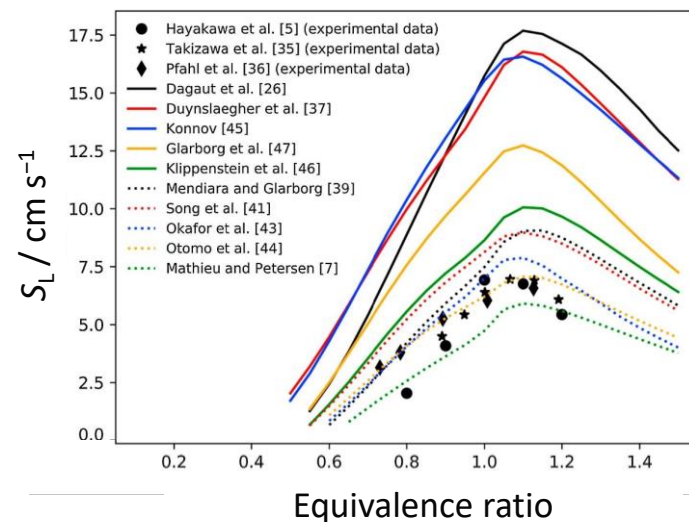
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- **Disadvantageous combustion characteristics of pure NH_3**
 $\Rightarrow$ **blending NH_3 with other fuels such as H_2 , CO , CH_4**
- Accurate chemical kinetic models $\rightarrow$ **development, design**
- **Several models are available** in the literature:
 - models are usually not good under all experimental conditions
 - disagreement between different models
- **Comprehensive validation and further development of these models are needed.**



R. C. da Rocha et al., *Fuel* 246 (2019) 24–33

- Investigation of the **current state of the chemical kinetic modeling of the combustion of NH_3/H_2 and NH_3 /syngas fuel mixtures** under a wide range of combustion conditions.
- **Main steps** of the investigation:
 - 1) **Collection of a large set of experimental data** from the literature.
 - 2) **Utilization of recent combustion mechanisms** from the literature.
 - 3) **Assessing the performances of the mechanisms quantitatively.**
 - 4) Investigation of the best-performing models by **sensitivity analysis to identify model parameters most influential on simulation outputs.**

Experimental data collection

- Types of experiments investigated in this study:

Facility	Measured quantity
Spatially homogeneous (0D) reactors	
Shock Tube (ST)	ignition delay time (IDT)
Jet Stirred Reactor (JSR)	concentrations of species (conc)
Flow Reactor (FR)	concentrations of species (conc)
Spatially 1D reactors (investigation of flames)	
Laminar Premixed Flames	laminar burning velocity (LBV)

- Literature has been reviewed extensively.
- Experimental data were utilized from **31 publications**.

Experimental data collection

- Collected experimental data were encoded in **XML data files of ReSpecTh Kinetic Data (RKD) format [1]**.
 - Each measurement is stored in a separate XML data file.
 - One XML data file may contain more than one experimental dataset.

Exp. type	XMLs	Datasets	Data points	T / K	p / atm	φ
NH₃/H₂ combustion						
ST-IDT	26	26	200	1022–2489	1.01–41.65	0.50–2.00
JSR-conc	32	113	1651	500–1452	1.00–1.20	0.01–1.50
FR-conc	24	89	1141	451–1973	1.00–98.69	0.00–2.44
LBV	129	129	850	298–476	0.50–10.00	0.40–1.80
<u>Subtotal:</u>	<u>211</u>	<u>357</u>	<u>3842</u>			
NH₃/syngas combustion						
JSR-conc	8	40	229	900–1350	1.00	0.38–1.51
FR-conc	1	2	18	873–1273	1.00	0.01
LBV	80	80	881	298–443	1.00–10.00	0.70–1.70
<u>Subtotal:</u>	<u>89</u>	<u>122</u>	<u>1128</u>			
<u>Total:</u>	<u>300</u>	<u>479</u>	<u>4970</u>			

[1] T. Varga et al., ReSpecTh Kinetics Data Format Specification v2.3, <http://respecth.hu/>

Reaction mechanisms investigated

- 18 mechanisms were investigated in this study.

Mechanism ID	H/O/N part		H/O/N + C1 part		Wet CO submech	He species	Ref.
	Species	Reactions	Species	Reactions			
Tian-2009	31	191	60	508	✓	✗	[2]
Mathieu-2015	33	159	52	273	✓	✓	[3]
GDFKin-2016	22	124	45	350	✓	✗	[4]
Nakamura-2017	34	229	—	—	✗	✓	[5]
SanDiego-2018	21	64	33	129	✓	✓	[5]
Otomo-2018	32	213	—	—	✗	✓	[7]
Glarborg-2018	33	211	80	674	✓	✓	[8]
Okafor-2018	25	101	46	262	✓	✗	[9]
POLIMI-2020	31	203	—	—	✗	✓	[10]
NUIG-2020	37	231	43	253	✓	✓	[11]
Han-2020	32	163	35	177	✓	✓	[12]
Mei-2020	34	237	38	255	✓	✓	[13]
Konnov-2021	36	295	80	858	✓	✓	[14]
KAUST-2021	34	262	—	—	✗	✓	[15]
Shrestha-2021	33	262	63	609	✓	✓	[16]
Mei-2021	35	239	39	257	✓	✓	[17]
Zhou-2021	32	187	34	197	✓	✗	[18]
Gotama-2022	32	165	—	—	✗	✓	[19]

Reaction mechanisms investigated



- [2] Z. Tian et al., *Combust. Flame* 156 (2009) 1413–1426.
- [3] O. Mathieu and E. L. Petersen, *Combust. Flame* 162 (2015) 554–570.
- [4] N. Lamoureux et al., *Combust. Flame* 163 (2016) 557–575.
- [5] H. Nakamura et al., *Combust. Flame* 185 (2017) 16–27.
- [6] <http://web.eng.ucsd.edu/mae/groups/combustion/mechanism.html>
- [7] J. Otomo et al., *Int. J. Hydrog. Energy* 43 (2018) 3004–3014.
- [8] P. Glarborg et al., *Prog. Energy Combust. Sci.* 67 (2018) 31–68.
- [9] E. C. Okafor et al., *Combust. Flame* 187 (2018) 185–198.
- [10] <http://creckmodeling.chem.polimi.it/menu-kinetics/menu-kinetics-special-mechanisms> (NH₃ mechanism)
- [11] Q.-D. Wang et al., *Energy Fuels* 34 (2020) 949–964.
- [12] X. Han et al., *Combust. Flame* 213 (2020) 1–13.
- [13] B. Mei et al., *Combust. Flame* 220 (2020) 368–377.
- [14] M. L. Lavadera and A. A. Konnov, *Combust. Flame* 225 (2021) 65–73.
- [15] X. Zhang et al., *Combust. Flame* 234 (2021) 111653.
- [16] K. P. Shrestha et al., *Proc. Combust. Inst.* 38 (2021) 2163–2174.
- [17] B. Mei et al., *Combust. Flame* 231 (2021) 111472.
- [18] S. Zhou et al., *Combust. Flame* 233 (2021) 111594.
- [19] G. J. Gotama et al., *Combust. Flame* 236 (2022) 111753.

- **Optima++ framework [20]**
 - easy testing and comparison of the performance of mechanisms
 - required input files:
 - XML format file containing the experimental data
 - plain text CHEMKIN-format mechanism file
 - Optima++ is able to utilize several simulation packages (OpenSMOKE++, FlameMaster, CANTERA, Zero-RK)
 - **OpenSMOKE++ [21]** was used in this work
 - all reactor models are available that are needed

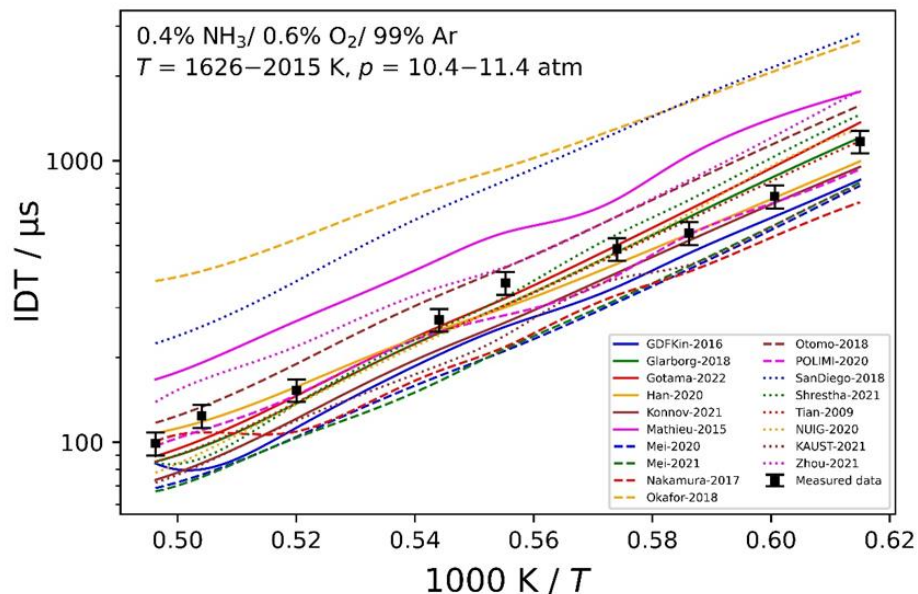
[20] M. Papp et al., Computer programs for the analysis, optimization and reduction of reaction mechanisms – Optima++. <http://respecth.hu>

[21] The CRECK Modeling Group (Politecnico di Milano), OpenSMOKE++. <https://www.opensmokepp.polimi.it/>

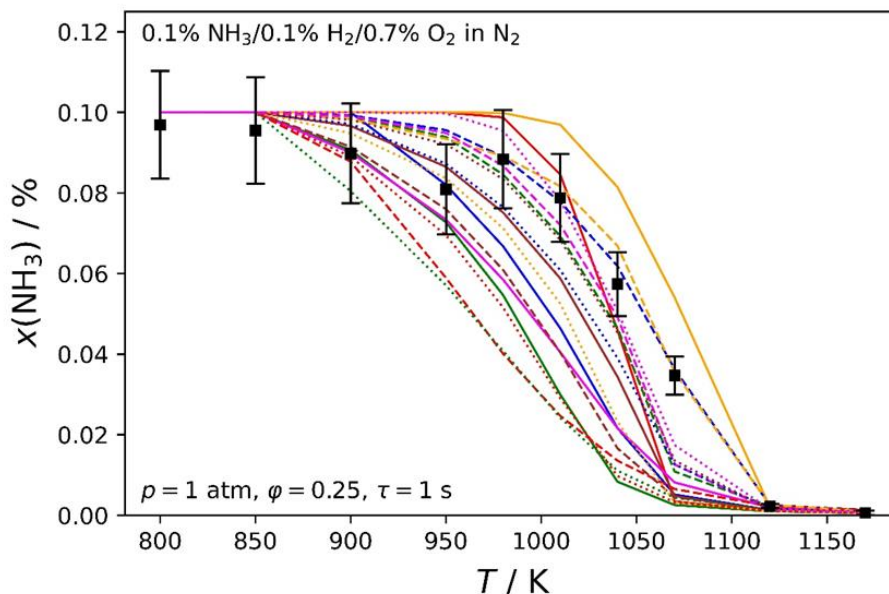
Mechanism testing and comparison

- The investigated models have very different performances.

ST-IDT measurement by Mathieu et al. [3]



JSR-conc measurement by Zhang et al. [15]



A quantitative method is needed to assess the goodness of mechanisms on a large set of data!

[3] O. Mathieu and E. L. Petersen, *Combust. Flame* 162 (2015) 554–570.

[15] X. Zhang et al., *Combust. Flame* 234 (2021) 111653.

- An **averaged error function** is defined:

$$E_{ij} = \left(\frac{Y_{ij}^{\text{sim}} - Y_{ij}^{\text{exp}}}{\sigma(Y_{ij}^{\text{exp}})} \right)^2 \longrightarrow E = \frac{1}{N_{\text{XML}}} \sum_{i=1}^N \frac{1}{N_i} \cdot \frac{1}{N_{\text{ds},i}} \sum_{j=1}^{N_i} E_{ij}$$

$$Y_{ij} = \begin{cases} y_{ij} & \text{if } \sigma(y_{ij}^{\text{exp}}) \approx \text{constant} \\ \ln y_{ij} & \text{if } \sigma(\ln(y_{ij}^{\text{exp}})) \approx \text{constant} \end{cases}$$

$$E = 9$$

↓

3 σ error on average

- N_{XML} : Number of XML data files
- N : Number of datasets
- N_i : number of data points in the i -th dataset
- $N_{\text{ds},i}$: Number of datasets in the XML of the i -th dataset
- y_{ij}^{exp} : measured value of the j -th experimental data point in the i -th dataset
- y_{ij}^{sim} : simulation result for the j -th experimental data point in the i -th dataset
- $\sigma(Y_{ij}^{\text{exp}})$: standard deviation of Y_{ij}^{exp}

- Basic principle:

Mechanisms are compared using the same set of data points.

+ unbiased comparison is desired



Some data points need to be excluded!

- **Three-step data filtering process:**

Exclude data point if

- 1) Simulation did not converge with *at least one* mechanism.
It is an indicator of the robustness of the corresponding mechanism(s).
- 2) $E_{ij} > 9$ with *each* of the investigated mechanisms.
- 3) $E_{ij} > 400$ with *at least one* mechanism.
It is an indicator of the performance of the corresponding mechanism(s)
(in addition to E).

Quantitative mechanism comparison

Results and discussion: NH_3/H_2 fuel mixtures without He



Data filtration	ST-IDT	JSR-conc	FR-conc	LBV	Overall
All points:	200	1589	1003	843	3635
Included points:	140	787	817	638	2382
Included (%):	70.0%	49.5%	81.5%	75.7%	65.5%
Mechanism ID	$E_{\text{ST-IDT}}$	$E_{\text{JSR-conc}}$	$E_{\text{FR-conc}}$	E_{LBV}	E_{overall}
KAUST-2021	17.5	5.1	2.9	6.9	8.1
POLIMI-2020	10.4	8.6	6.9	7.0	8.2
Han-2020	11.7	11.4	8.9	5.1	9.3
Shrestha-2021	11.2	17.3	6.2	7.3	10.5
Gotama-2022	19.3	10.3	8.3	5.4	10.8
Otomo-2018	9.5	8.6	6.6	18.7	10.9
Tian-2009	9.1	11.6	7.9	14.9	10.9
Konnov-2021	10.5	16.6	8.2	9.0	11.1
Mei-2021	28.6	5.0	9.0	6.0	12.1
Mei-2020	28.6	5.9	9.1	5.2	12.2
Mathieu-2015	23.8	9.2	6.5	22.1	15.4
NUIG-2020	15.5	15.3	10.5	23.4	16.2
Zhou-2021	40.5	8.3	8.4	13.7	17.7
Nakamura-2017	27.0	25.8	7.5	11.5	18.0
SanDiego-2018	48.4	10.1	10.7	11.1	20.1
Glarborg-2018	10.3	13.2	4.7	53.2	20.3
Okafor-2018	121.7	11.3	10.9	22.2	41.5
GDFKin-2016	28.3	12.8	7.6	127.6	44.1

Quantitative mechanism comparison

Results and discussion: NH₃/syngas fuel mixtures



Data filtration	Conc (JSR + FR)	LBV	Overall
All points:	247	881	1128
Included points:	189	858	1047
Included (%):	76.5%	97.4%	92.8%
Mechanism ID	E_{conc}	E_{LBV}	E_{overall}
Mei-2021	4.6	9.4	7.0
Mei-2020	5.5	9.1	7.3
Shrestha-2021	6.7	9.3	8.0
Han-2020	13.0	11.0	12.0
NUIG-2020	8.8	17.3	13.1
Mathieu-2015	5.2	21.0	13.1
Konnov-2021	13.2	17.3	15.3
Zhou-2021	11.9	20.9	16.4
SanDiego-2018	5.7	29.2	17.5
Tian-2009	9.1	38.9	24.0
Okafor-2018	9.2	62.7	35.9
GDFKin-2016	4.5	70.0	37.2
Glarborg-2018	4.1	81.6	42.8

Local sensitivity analysis

- The best-performing models were further investigated by **brute force local sensitivity analysis** [23].
- **Local sensitivity coefficients** were computed for
 - **kinetic parameters:**
A preexponential factor of each rate coefficient was perturbed by +5%
 - **thermodynamic parameters:**
 $c_{p,k}^{\ominus}$, $\Delta_f H_k^{\ominus}$, $S_k^{\ominus}$ for each species k [24]
- More details, results and discussion:
see our future publications.

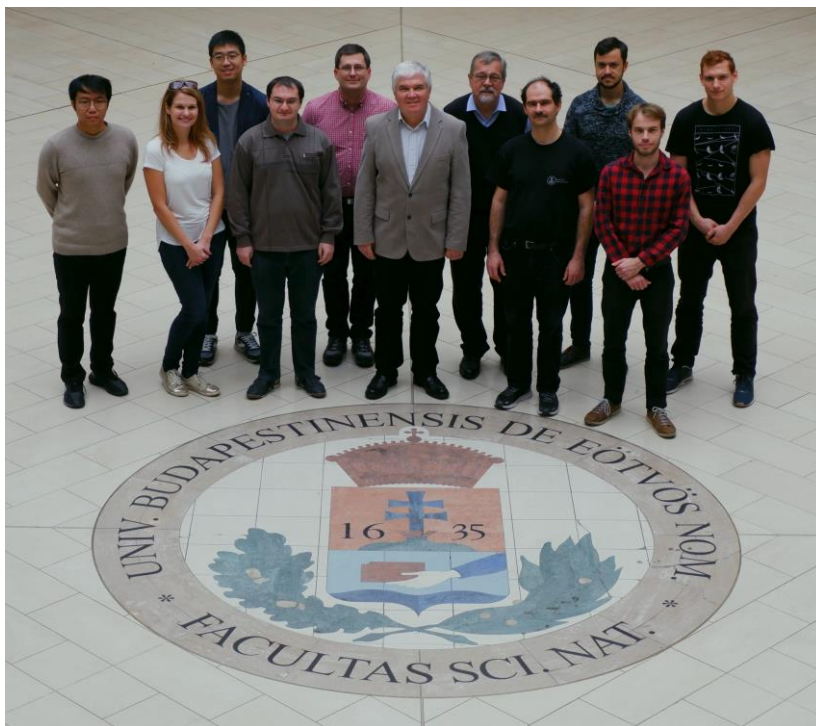
[23] T. Turányi, A. S. Tomlin, *Analysis of Kinetic Reaction Mechanisms*. Berlin, Heidelberg; Springer, 2014.

[24] M. Kovács et al., *IJCK* 53 (2021) 884–900.

Summary and outlook

- **Large set of experimental data** (ca. 5000 data points) was collected for **NH_3/H_2 and $\text{NH}_3/\text{syngas}$ combustion.**
- The performances of **18 detailed reaction mechanisms were quantitatively tested** against the experimental data.
 - NH_3/H_2 : KAUST-2021 and POLIMI-2020 are the best
 - $\text{NH}_3/\text{syngas}$: Mei-2021, Mei-2020, and Shrestha-2021 are the best
- **Significant differences** were found **between** the performances of **the different models.**
- **The overall performances of the models should be improved significantly.**
- Results presented in this work may facilitate further mechanism development for NH_3/H_2 and $\text{NH}_3/\text{syngas}$ combustion systems.

Thank you for your attention!



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<https://ChemKinLab.ELTE.hu>

Quantitative mechanism comparison

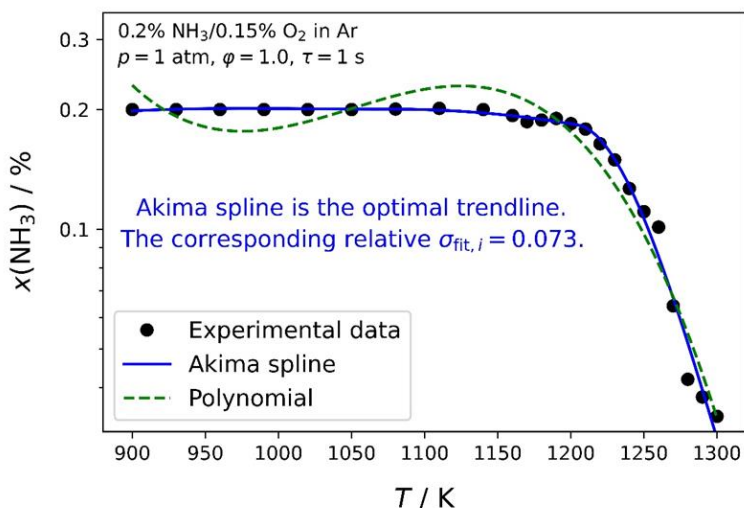
The standard deviation of experimental data



- Two uncertainty sources are considered:

$$\sigma(Y_{ij}^{\text{exp}}) = \sqrt{\sigma_{\text{fit},i}^2 + \sigma_{\text{exp},ij}^2}$$

- $\sigma_{\text{exp},ij}$: standard deviation of the experimental uncertainty
- $\sigma_{\text{fit},i}$: estimated statistical scatter of the i -th dataset
- $\sigma_{\text{fit},i}$ was obtained by **fitting a trendline** (spline or polynomial function) **to the data points** of the i -th dataset [22]



- To find the optimal trendline and the corresponding $\sigma_{\text{fit},i}$ code **Minimal Spline Fit** [22] was used
- Visual inspection of the fitted function graphs is always needed!

[22] T. Nagy and T. Turányi, ECM; 2021; 14-15 April; Naples, Italy. Paper 336.

Local sensitivity analysis

- The best-performing models were further investigated by **brute-force local sensitivity analysis** [23]
- **Local sensitivity coefficients** (s_{ij}) were computed for
 - kinetic parameters (A preexponential factors were perturbed by +5%)
 - thermodynamic parameters ($c_{p,k}^\ominus$, $\Delta_f H_k^\ominus$, $S_k^\ominus$ for each species k) [24]
- s_{ij} -s were normalized: $sn_{ij} = \frac{p_j}{Y_i} \cdot s_{ij}$
- sn_{ij} -s were scaled into the $[-1, 1]$ interval for each data point i :

$$-1 \leq \widetilde{sn}_{ij} = \frac{sn_{ij}}{\max_j \{|sn_{ij}|\}} \leq 1$$

- **A sensitivity coefficient is considered significant if:** $|\widetilde{sn}_{ij}| \geq 0.1$

[23] T. Turányi, A. S. Tomlin, *Analysis of Kinetic Reaction Mechanisms*. Berlin, Heidelberg; Springer, 2014.

[24] M. Kovács et al., *IJCK* 53 (2021) 884–900.

- **Main conclusions:**
 - Though the investigated models have different parameter sets, **the most important reactions and thermodynamic properties are similar**
 - The **most important reactions are not the same for the different types of experiments** but most of them include the NH_3 , NH_2 , and/or NNH species
 - Among the **thermodynamic parameters**, model outputs are most sensitive to the **data of NH_3 and NH_2**
- More details: **see our future publications**

- Example:**

10-10 most sensitive reactions for ST-IDT experiments with NH_3/H_2 fuel mixtures in POLIMI-2020 and KAUST-2021 mechanisms

POLIMI-2020			KAUST-2021	
Nr.	Reaction	Freq.	Reaction	Freq.
1	$\text{O}_2 + \text{H} = \text{OH} + \text{O}$	91.4%	$\text{O}_2 + \text{H} = \text{OH} + \text{O}$	78.7%
2	$\text{NH}_3 + \text{H} = \text{NH}_2 + \text{H}_2$	56.9%	$\text{NH}_2 + \text{NO} = \text{N}_2 + \text{H}_2\text{O}$ (DUP1)	62.4%
3	$\text{NH}_2 + \text{HO}_2 = \text{NH}_3 + \text{O}_2$	55.8%	$\text{NH}_2 + \text{NO} = \text{NNH} + \text{OH}$	62.4%
4	$\text{NH}_2 + \text{NO} = \text{NNH} + \text{OH}$	54.3%	$\text{NH}_2 + \text{HO}_2 = \text{NH}_3 + \text{O}_2$	59.9%
5	$\text{NH}_2 + \text{NH} = \text{N}_2\text{H}_2 + \text{H}$	53.8%	$\text{NH}_2 + \text{HO}_2 = \text{H}_2\text{NO} + \text{OH}$	52.3%
6	$\text{NH}_2 + \text{O}_2 = \text{H}_2\text{NO} + \text{O}$	51.3%	$\text{NH}_2 + \text{NO} = \text{N}_2 + \text{H}_2\text{O}$ (DUP2)	52.3%
7	$\text{NH}_3 + \text{OH} = \text{H}_2\text{O} + \text{NH}_2$	42.6%	$\text{NH}_3 + \text{H} = \text{NH}_2 + \text{H}_2$	51.8%
8	$\text{NH}_2 + \text{NO} = \text{N}_2 + \text{H}_2\text{O}$	41.6%	$\text{N}_2\text{H}_2 + \text{M} = \text{NNH} + \text{H} + \text{M}$	51.3%
9	$\text{NH}_3 = \text{NH}_2 + \text{H}$ (PLOG03)	40.6%	$\text{NH}_3 + \text{NH}_2 = \text{N}_2\text{H}_3 + \text{H}_2$	50.8%
10	$\text{O} + \text{OH} + \text{M} = \text{HO}_2 + \text{M}$	39.6%	$\text{N}_2\text{H}_2 + \text{H} = \text{NNH} + \text{H}_2$	46.7%