Progress in ~~Nitrogen~~ Novel Combustion Chemistry

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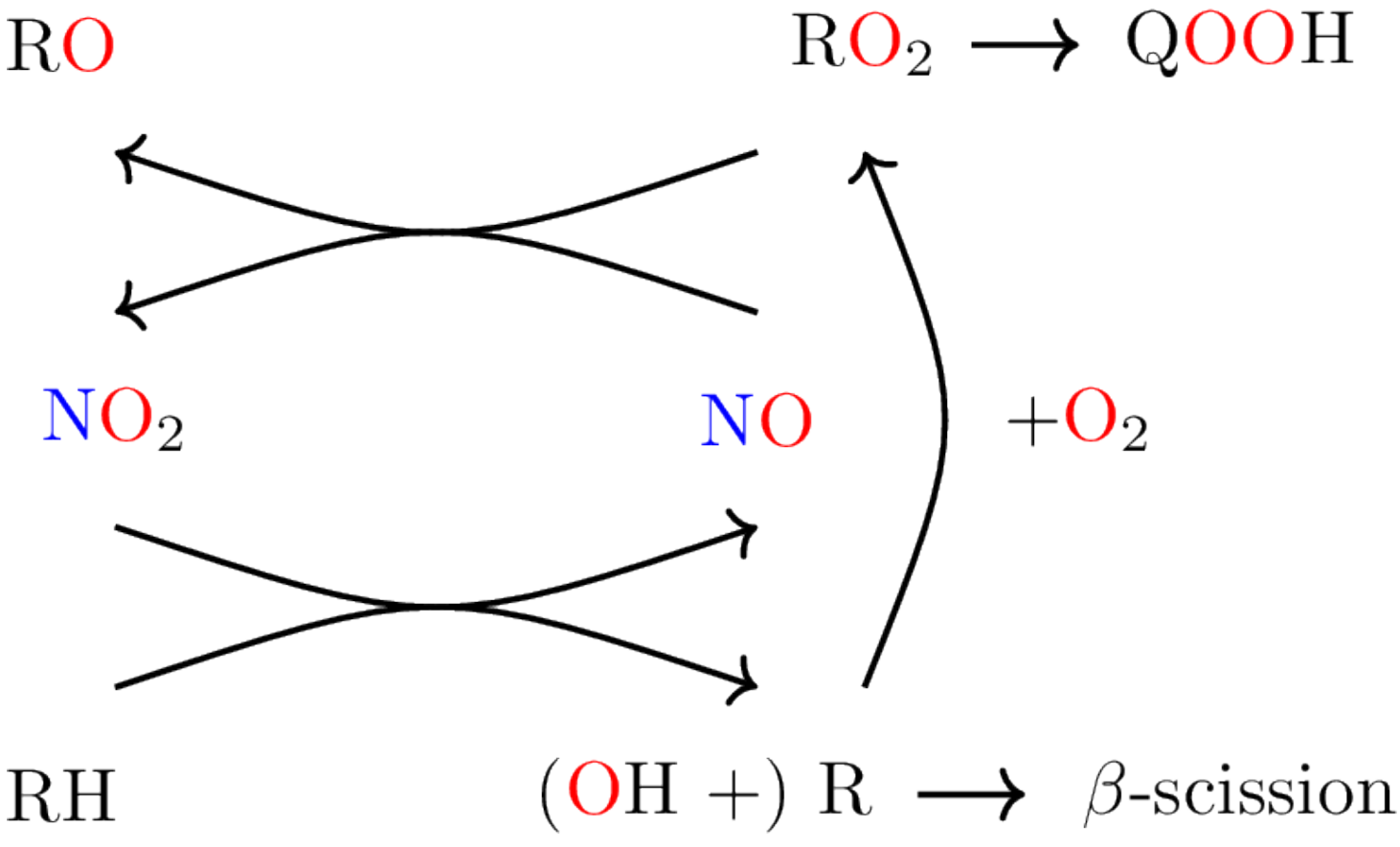
Physico-Chemical Fundamentals of Combustion

6. Januar 2021

NO_x interactions in hydrocarbon combustion



And when RH is replaced with QOOH or OOQOOH?

Latest revisions

- **The HNO_2 potential energy surface (PES) reactions calculated by Chen *et al.*[1]**
- **Rates for the H_2NO_2 and CH_4NO_2 PES from Fuller and Goldsmith[2]**
- **Hydrogen abstraction by NO_2 from alkanes and alkenes refit to the exothermic direction[3]**
- **Decomposition rates for alkyl nitrites[4], and isopropyl nitrate[5]**

[1] Chen, X. u. a. Reaction Chemistry & Engineering **2019**, *4*, 323–333.

[2] Fuller, M. E.; Goldsmith, C. F. Proceedings of the Combustion Institute **2019**, *37*, 695–702.

[3] Fuller, M. E.; Goldsmith, C. F. Proceedings of the Combustion Institute **2019**, *37*, 695–702, Fuller, M. E. u. a. Combustion and Flame **2021**, In preparation.

[4] Randazzo, J. B. u. a. Proceedings of the Combustion Institute **2019**, *37*, 703–710.

[5] Fuller, M. E.; Goldsmith, C. F. The Journal of Physical Chemistry A **2019**, *123*, 5866–5876.

Reaction Classes and Examples

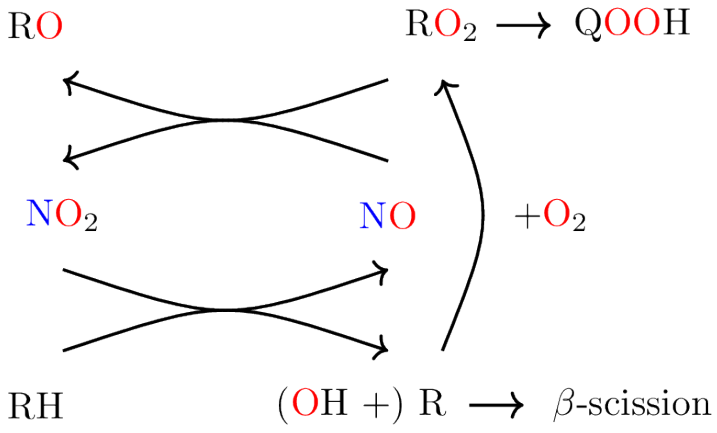
Develop mechanism by systematic inclusion of reaction classes

- **Hydrogen abstractions by NO_x to form HONO, HNO_2, HNO**
- **Unimolecular conformer formation and dissociation**
  - → $RNO_2 \rightleftharpoons R + NO_2$
  - → $RONO \rightleftharpoons RO + NO$
  - → $RONO_2 \rightleftharpoons RO + NO_2$
- **Isomerizations**
  - → $RONO \rightleftharpoons RNO_2$
- **Concerted HONO elimination**
  - → $RONO \rightleftharpoons$ alkene + HONO
- **NO_x cycling reactions**
  - → $RO_2 + NO \rightleftharpoons RO + NO_2$
  - → $RO + NO \rightleftharpoons R + NO_2$

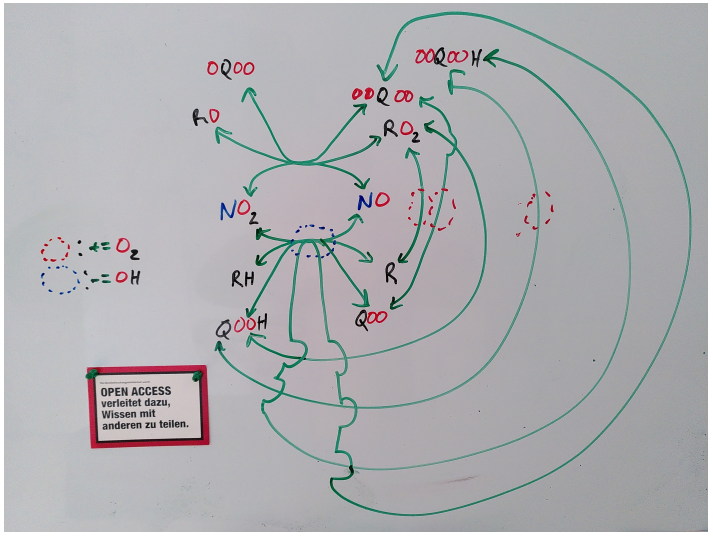
The old (slow) way forward

1. **Calculate sensitivities**
2. **Tweak/add some rates***
3. **Run simulations**
4. **Feel sad and start over**

*Until this...



...becomes this (or worse!)



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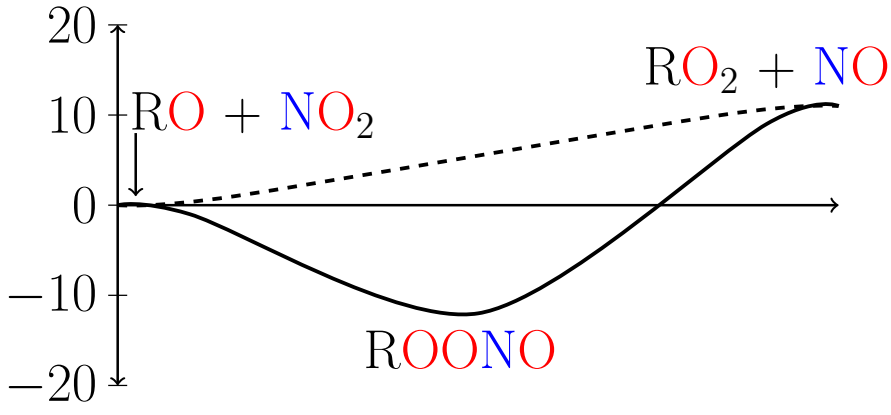
Progress on NO_x-Cycling



Generalized potential energy surface for alkoxy radical (RO) + NO_2 system. Energies in kcal/mol. Well-skipping occurs at virtually all combustion-relevant temperatures and pressures.

Reaction	A	n	E_a
$CH_3O_2 + NO \rightleftharpoons CH_3O + NO_2$	4.62E+15	-0.38	97.8
$C_2H_5O_2 + NO \rightleftharpoons C_2H_5O + NO_2$	2.11E+14	-0.12	-470.6
$NC_3H_7O_2 + NO \rightleftharpoons NC_3H_7O + NO_2$	1.07E+14	-0.25	-1302.0

Units: centimeters, kelvin, calories, moles

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