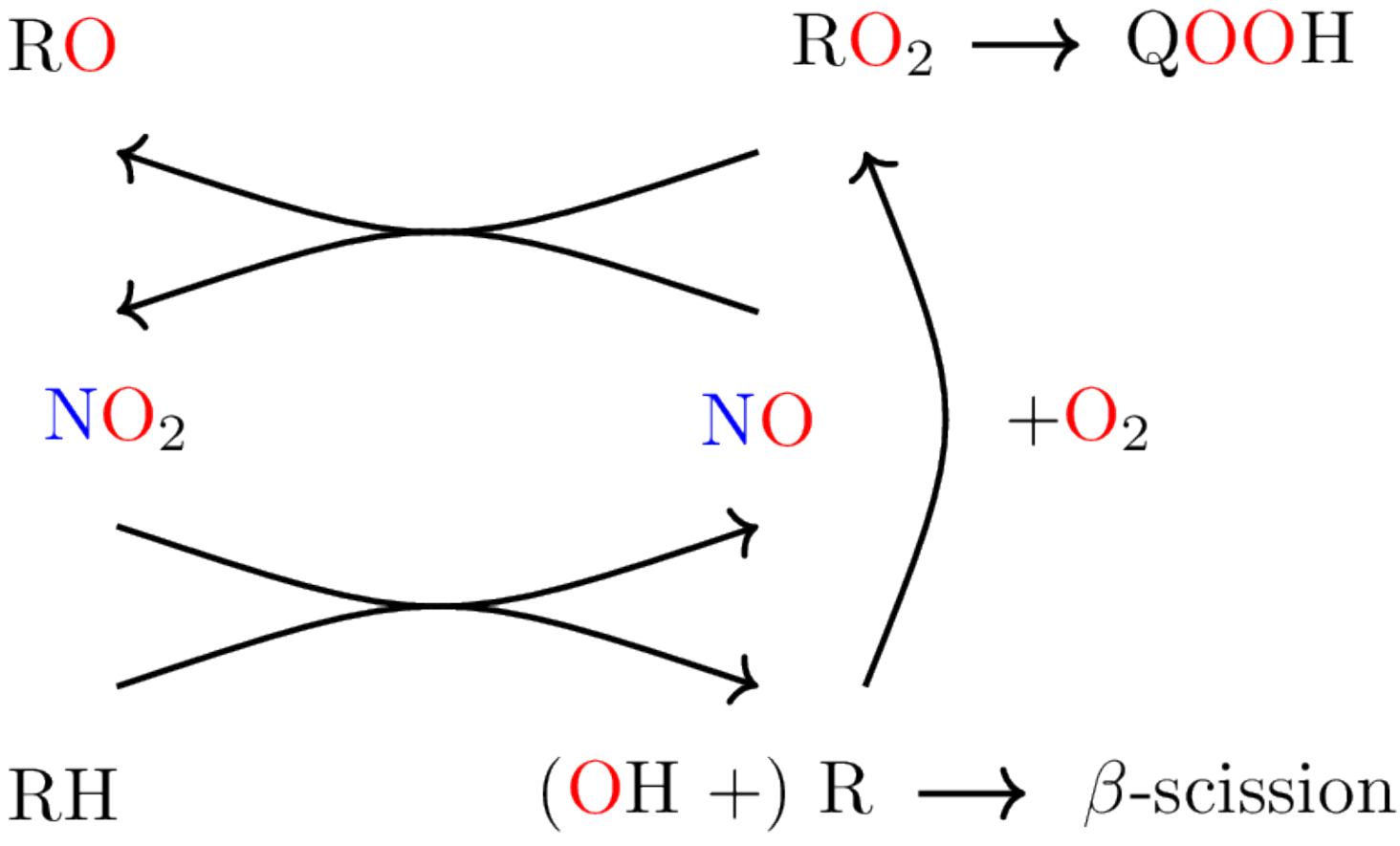
# Progress in ~~Nitrogen~~ Novel Combustion Chemistry

**Mark E. Fuller, Ph.D.**

Physico-Chemical Fundamentals of Combustion

30. 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.2019**.

[2] **Fuller.2018**.

[3] **Fuller.2018**, **Fuller.2020**.

[4] **Randazzo.2018**.

[5] **Fuller.2019.A**.

# Reaction Classes and Examples

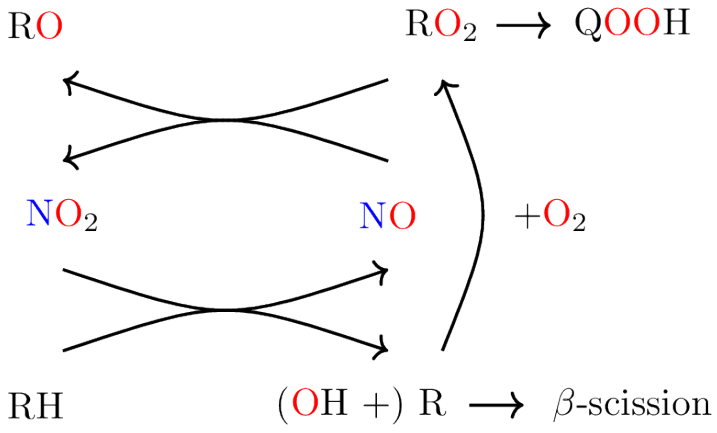
Develop mechanism by systematic inclusion of reaction classes

- **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**
  - → $RO_2 + NO \rightleftharpoons RO + NO_2$
  - → $RO + NO \rightleftharpoons R + NO_2$

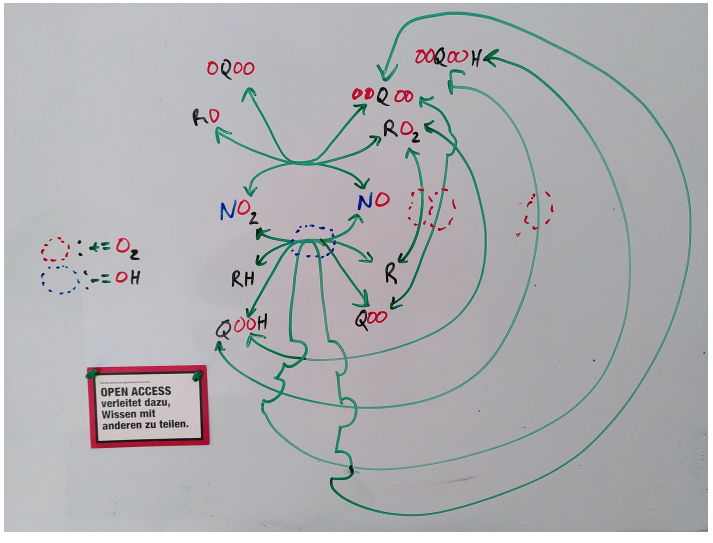
# The old (slow) way forward

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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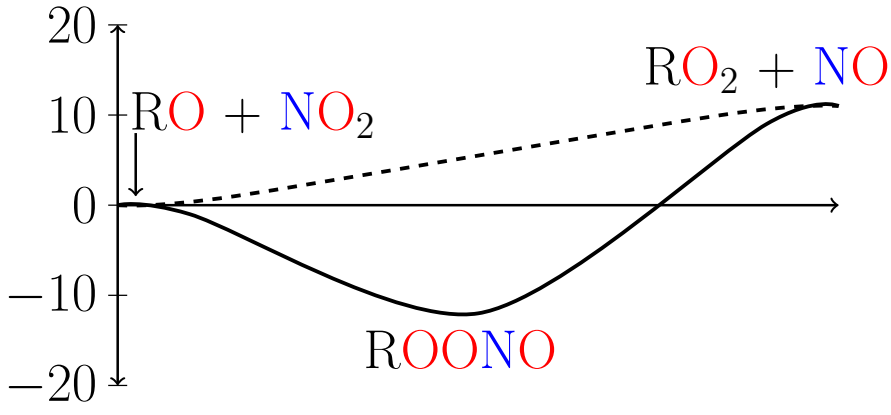
# Progress on $NO_x$-Cycling




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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