

Progress in ~~Nitrogen~~ Novel Combustion Chemistry

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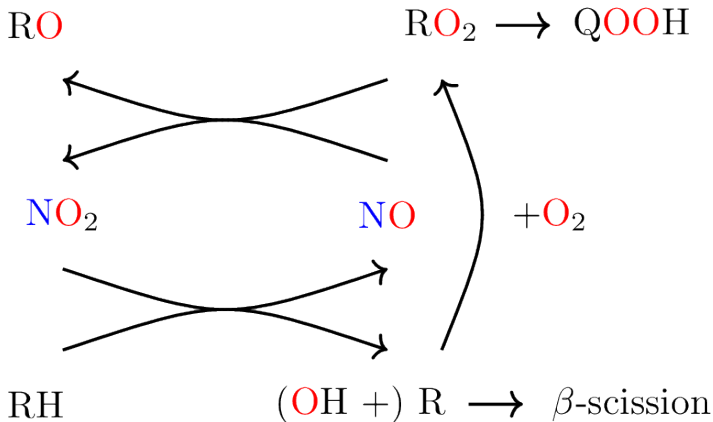
Physico-Chemical Fundamentals of Combustion

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NO_x interactions in hydrocarbon combustion



Physico-Chemical
Fundamentals of
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And when RH is replaced with QOOH or OOQOOH?

- 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 Goldsmith²
- Hydrogen abstraction by NO_2 from alkanes and alkenes refit to the exothermic direction³
- Decomposition rates for alkyl nitrites⁴, and isopropyl nitrate⁵

¹Chen.2019.

²Fuller.2018.

³Fuller.2018, Fuller.2020.

⁴Randazzo.2018.

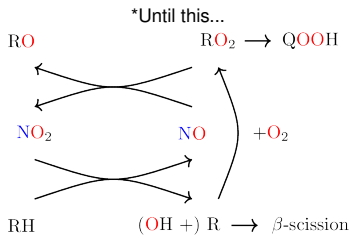
⁵Fuller.2019.A.

Develop mechanism by systematic inclusion of reaction classes

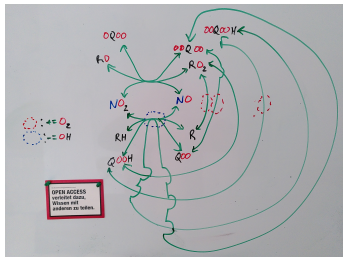
- **Hydrogen abstractions by NO_x to form HONO, HNO_2 , HNO**
- **Unimolecular conformer formation and dissociation**
 - $\text{RNO}_2 \rightleftharpoons \text{R} + \text{NO}_2$
 - $\text{RONO} \rightleftharpoons \text{RO} + \text{NO}$
 - $\text{RONO}_2 \rightleftharpoons \text{RO} + \text{NO}_2$
- **Isomerizations**
 - $\text{RONO} \rightleftharpoons \text{RNO}_2$
- **Concerted HONO elimination**
 - $\text{RONO} \rightleftharpoons \text{alkene} + \text{HONO}$
- **NO_x cycling reactions**
 - $\text{RO}_2 + \text{NO} \rightleftharpoons \text{RO} + \text{NO}_2$
 - $\text{RO} + \text{NO} \rightleftharpoons \text{R} + \text{NO}_2$

1. Calculate sensitivities

2. Tweak/add some rates*

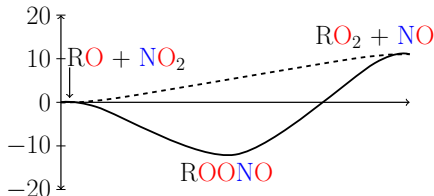


...becomes this (or worse!)



3. Run simulations

4. Feel sad and start over



Generalized potential energy surface for alkoxy radical (RO) + NO₂ system. Energies in kcal/mol. Well-skipping occurs at virtually all combustion-relevant temperatures and pressures.

Reaction	<i>A</i>	<i>n</i>	<i>E_a</i>
CH ₃ O ₂ + NO ⇌ CH ₃ O + NO ₂	4.62E+15	-0.38	97.8
C ₂ H ₅ O ₂ + NO ⇌ C ₂ H ₅ O + NO ₂	2.11E+14	-0.12	-470.6
NC ₃ H ₇ O ₂ + NO ⇌ NC ₃ H ₇ O + NO ₂	1.07E+14	-0.25	-1302.0

Units: centimeters, kelvin, calories, moles

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