# Chemical Kinetics Study on Ignition Process of Highly-Diluted Mixtures - How to Activate Slow Ignition Process -

Workshop 2012, UMC
December 4, Winc Aichi, Nagoya

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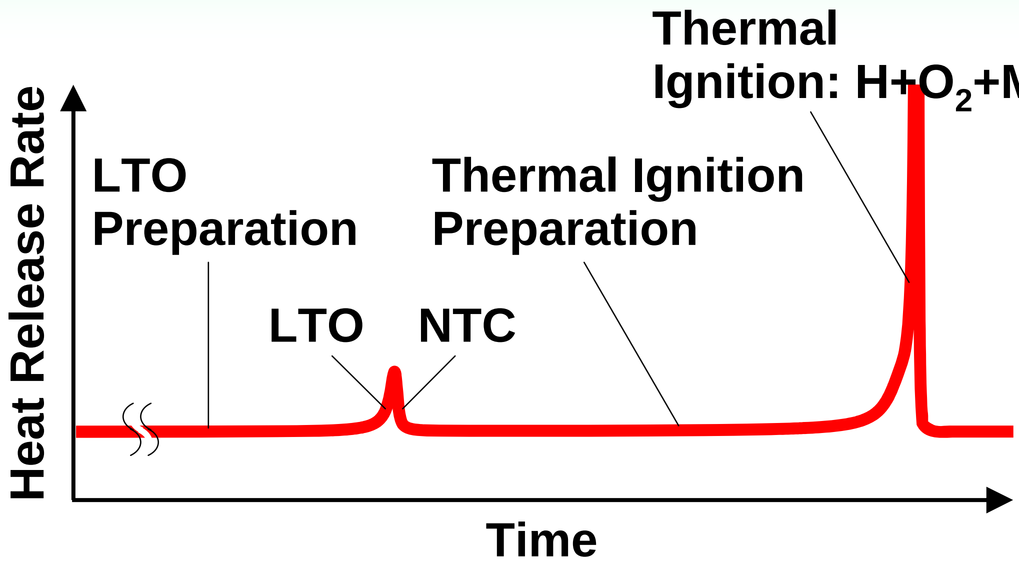
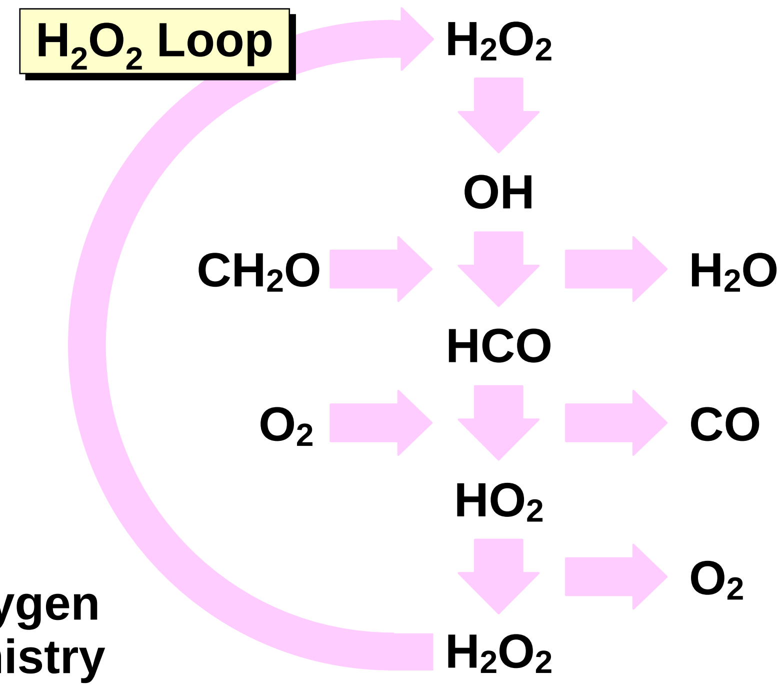
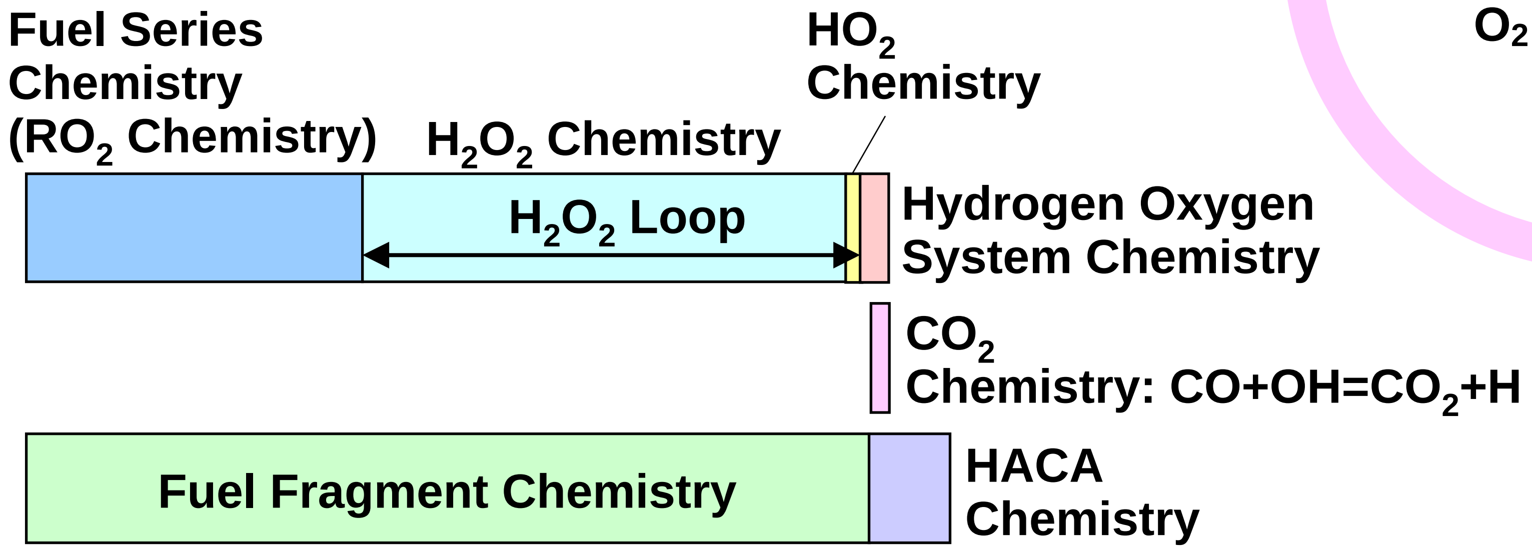
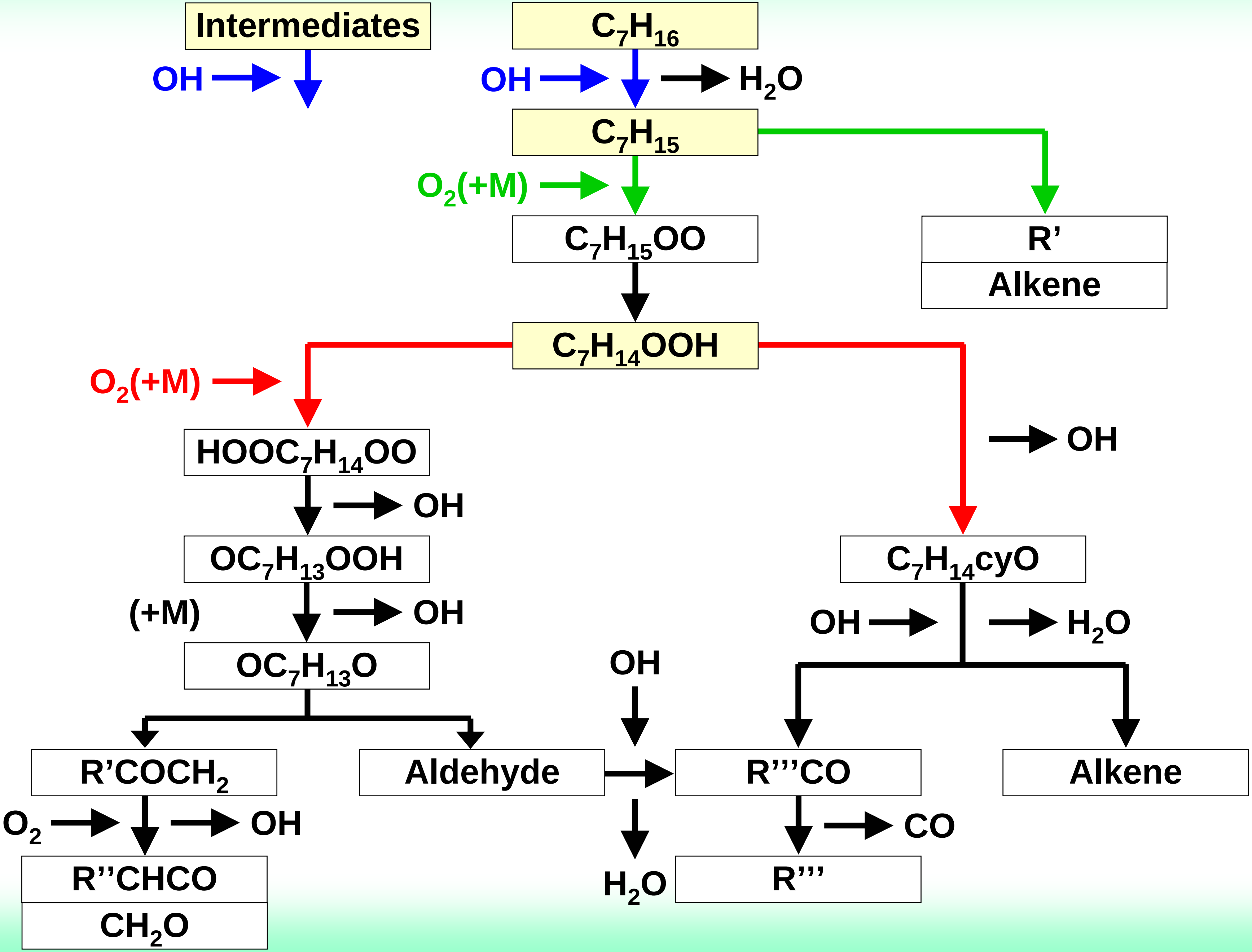
# Previous Studies Using Contribution Matrices



# Three Branches Controlling LTO Initiation and Termination



# $H_2O_2$ Loop Chemistry

**Main Loop**

$H_2O_2 + M \rightarrow 2OH + M - 216\ kJ$

$OH + CH_2O \rightarrow HCO + H_2O + 122\ kJ$

$HCO + O_2 \rightarrow HO_2 + CO + 138\ kJ$

$2HO_2 \rightarrow H_2O_2 + O_2 + 168\ kJ$

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$2CH_2O + O_2 \rightarrow 2H_2O + 2CO + 473\ kJ$

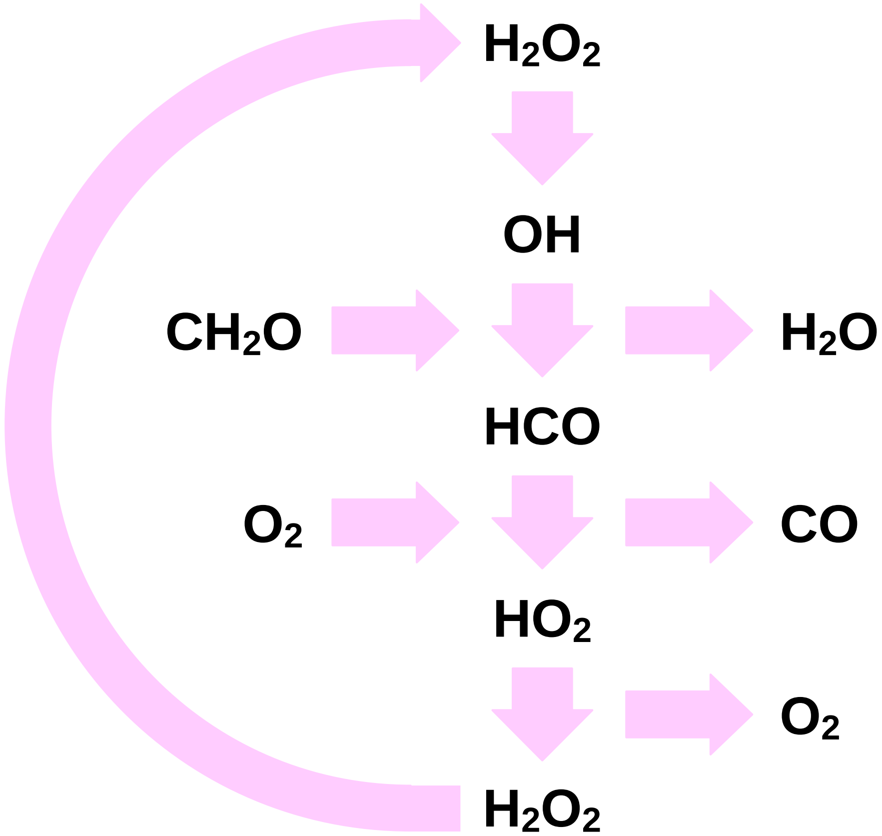
**Sub Reactions**

$H + O_2 + M \rightarrow HO_2 + M + 202\ kJ$

$H_2O_2 + OH \rightarrow HO_2 + H_2O + 130\ kJ$

$HO_2 + OH \rightarrow H_2O + O_2 + 297\ kJ$

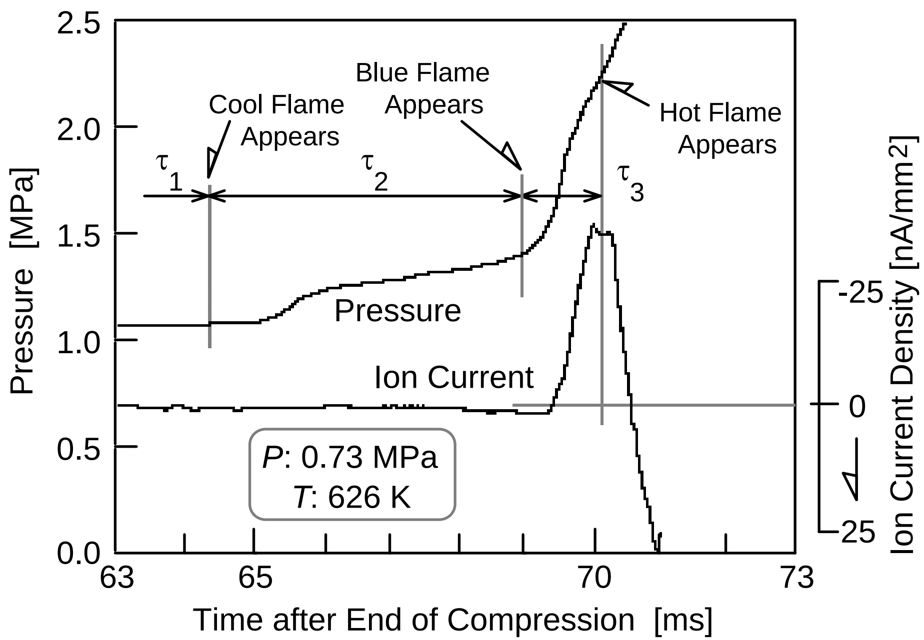
$HO_2 + CH_2O \rightarrow H_2O_2 + HCO - 7kJ$



# Motivations

1. **What is the final phase of ignition process of highly diluted mixtures like? Is it similar to the thermal ignition phase?**
   **How is CO oxidized into $CO_2$ at low temperatures?**

2. **Experimental data often show the two-stage main heat release in lean conditions.**
   **Why the two-stage heat release takes place?**



# What is KUCRS?



**KUCRS**

– Knowledge-basing Utilities for Complex Reaction Systems –





## What is KUCRS?

KUCRS (Knowledge-basing Utilities for Complex Reaction Systems) is a utility software library for the development of gas-phase chemical kinetic models of hydrocarbon oxidation or combustion reaction systems.

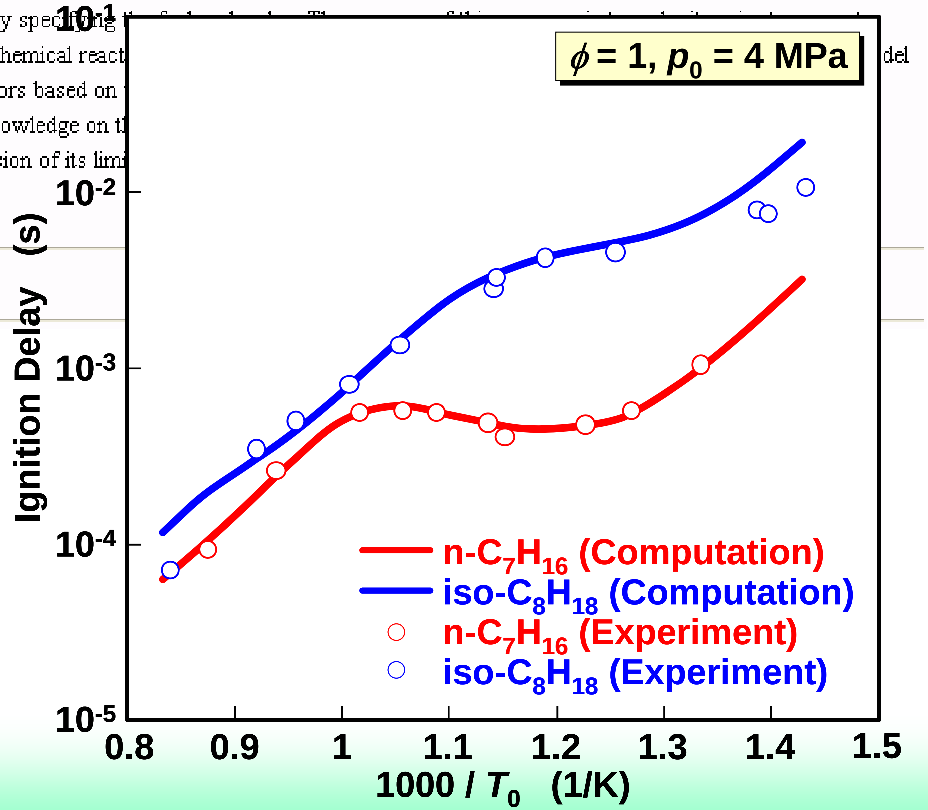
Hydrocarbon oxidation processes, such as combustion, are extremely complex chemical reaction systems. For example, the gasoline for automobile is a mixture of more than a hundred organic compounds. Furthermore, each *detailed kinetic model* to describe the combustion of a single pure alkane of $C_7$ to $C_8$, which is a component of gasoline, is said to requires thousands of chemical processes. This is because of the catenative nature of organic compounds.

On the other hand, this polymorphic nature of organic compounds allows us to estimate the properties from those of similar compounds by analogy. The applicability of such analogy can be seen, for example, from the success of the well-known Benson's *Group Additivity* methods.[1)] Unfortunately, though Benson himself indicated several excellent estimate for the reaction rate from analogy, the Group Additivity for the reaction rate is far from established, mainly because of the lack of quantitative and detailed knowledge on the chemical reactions.

A program called 'combust' developed based on KUCRS automatically generate a set of deteiled kinetic model by only spec… detaild kinetic mechanism based on the same *rules*. By using this program, the improvement of the knowledge on the chemical react… del with experiments. Needless to say, manual generation of thousands or tens of thousand chemical reactions without errors based on …

The ultimate form of the KUCRS is a software that can generate reliable detailed kinetic model without the detailed knowledge on t… course, the use of KUCRS is welcome for the simulation of many practical applications, provided with the comprehension of its limi… valuable information for improvement, is welcome.

1) S. W. Benson, *Thermochemical Kinetics, 2nd Ed.*, Wiley, New York, 1976.




**The pressure dependent rate constants of the $O_2$ addition to R and R'OOH, and the thermal decomposition of OR''OOH have been introduced.**

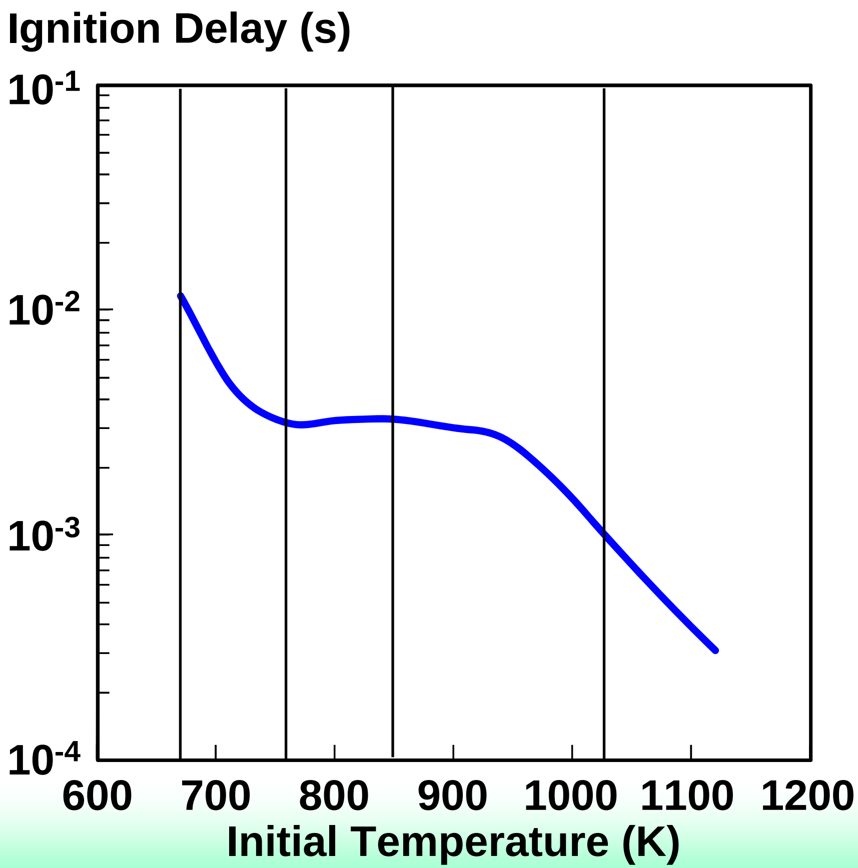
**$R+O_2(+M)=ROO(+M)$**

**$R'OOH+O_2(+M)=O_2R'OOH(+M)$**

**$OR''OOH(+M)=OR''O(+M)$**

# Computational Conditions

| | |
|---|---|
| **Kinetics Scheme** | **Detailed $n\text{-}C_7H_{16}$ Model Generated by KUCRS** |
| **Solver** | **CHEMKIN-PRO** |
| **Reactor** | **0 Dimensional Adiabatic Closed Constant-Volume** |
| **Mixtures** | **$n\text{-}C_7H_{16}$, $O_2$ and $N_2$** |
| **Base Values of Initial Concentrations** | **$n\text{-}C_7H_{16}$: 3.04 mol/m$^3$<br>$O_2$: 66.8 mol/m$^3$<br>$N_2$: 251 mol/m$^3$<br>Equivalent to Those in $n\text{-}C_7H_{16}$/Air Mixture at $\phi$: 0.5, $T_0$: 759 K and $p_0$: 2.027 MPa** |
| **Initial Temperature $T_0$** | **669, 759, 849, 1029 K** |
| **Initial Fuel Changed by** | **1/1, 1/2, 1/4** |
| **Initial $N_2$ Changed by** | **1/1, 2/1, 4/1** |



1. Effect of Dilution on Ignition Process

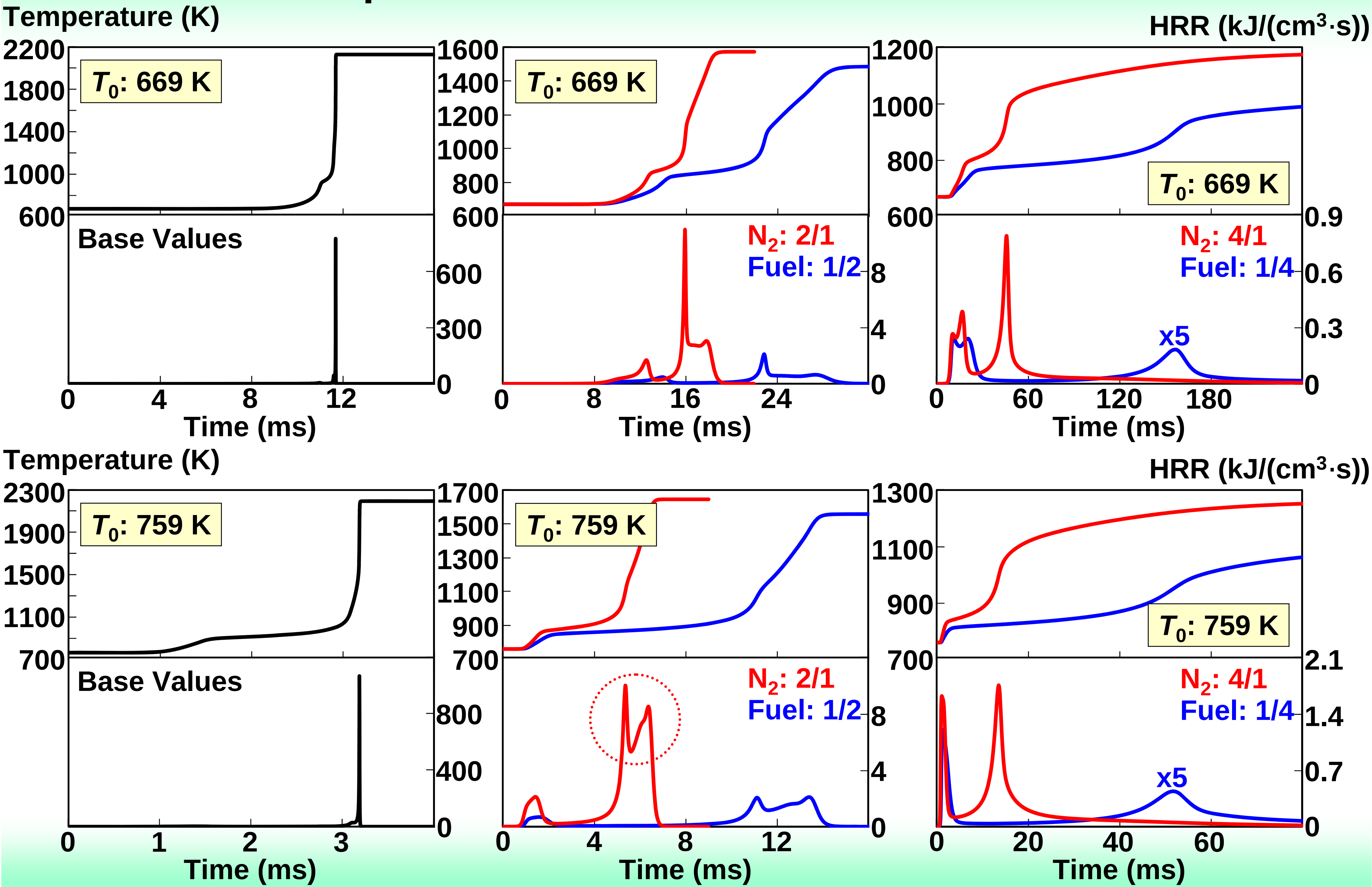
2. Two-Stage Main Heat Release of Highly-Diluted Mixtures

3. CO Chemistry of Highly-Diluted Mixtures

4. Ignition Process with High Initial Temperature

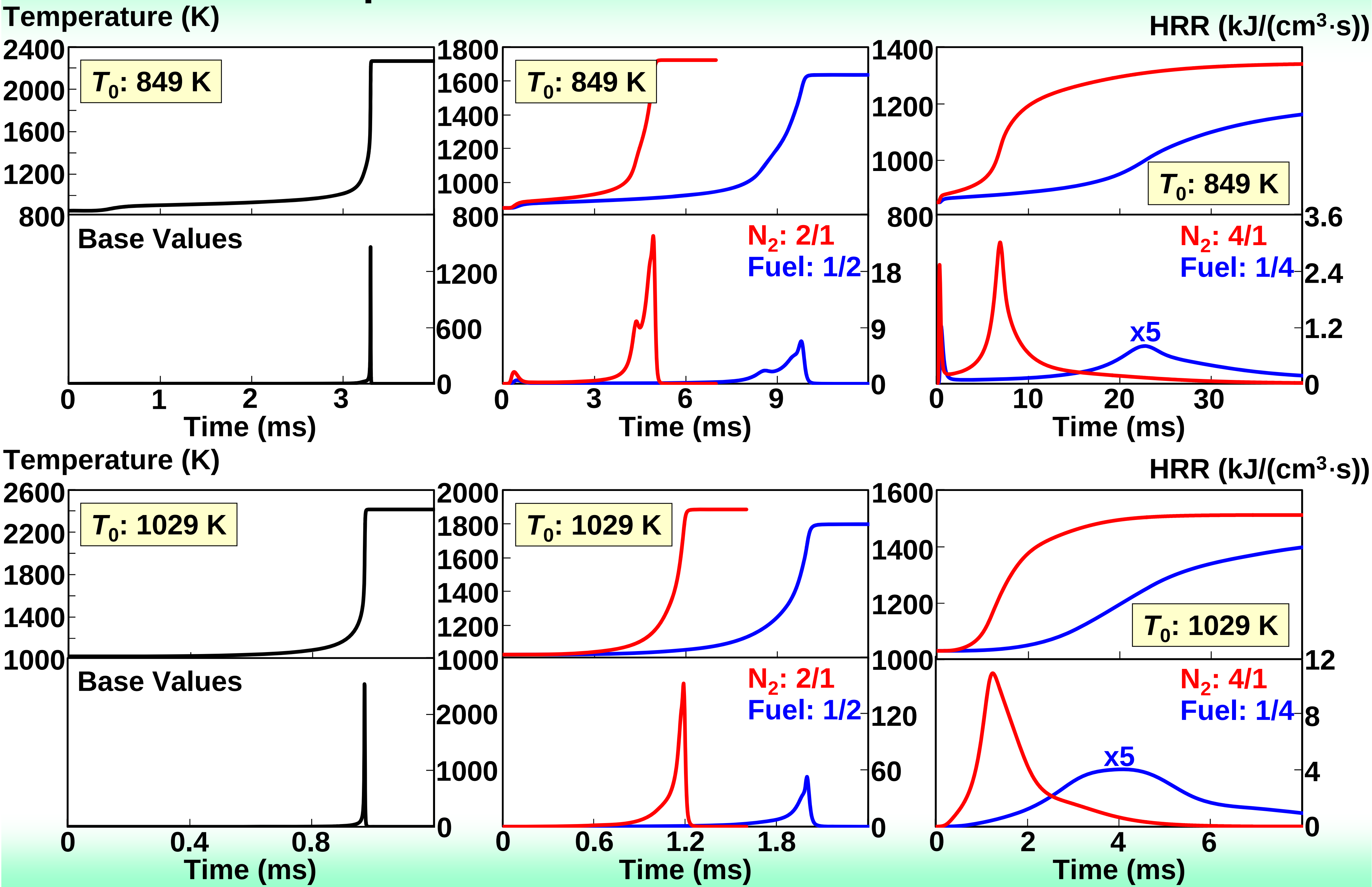
5. How to Activate Slow Ignition Process

# Histories of Temperature and Overall Heat Release Rate



# Histories of Temperature and Overall Heat Release Rate

No.10



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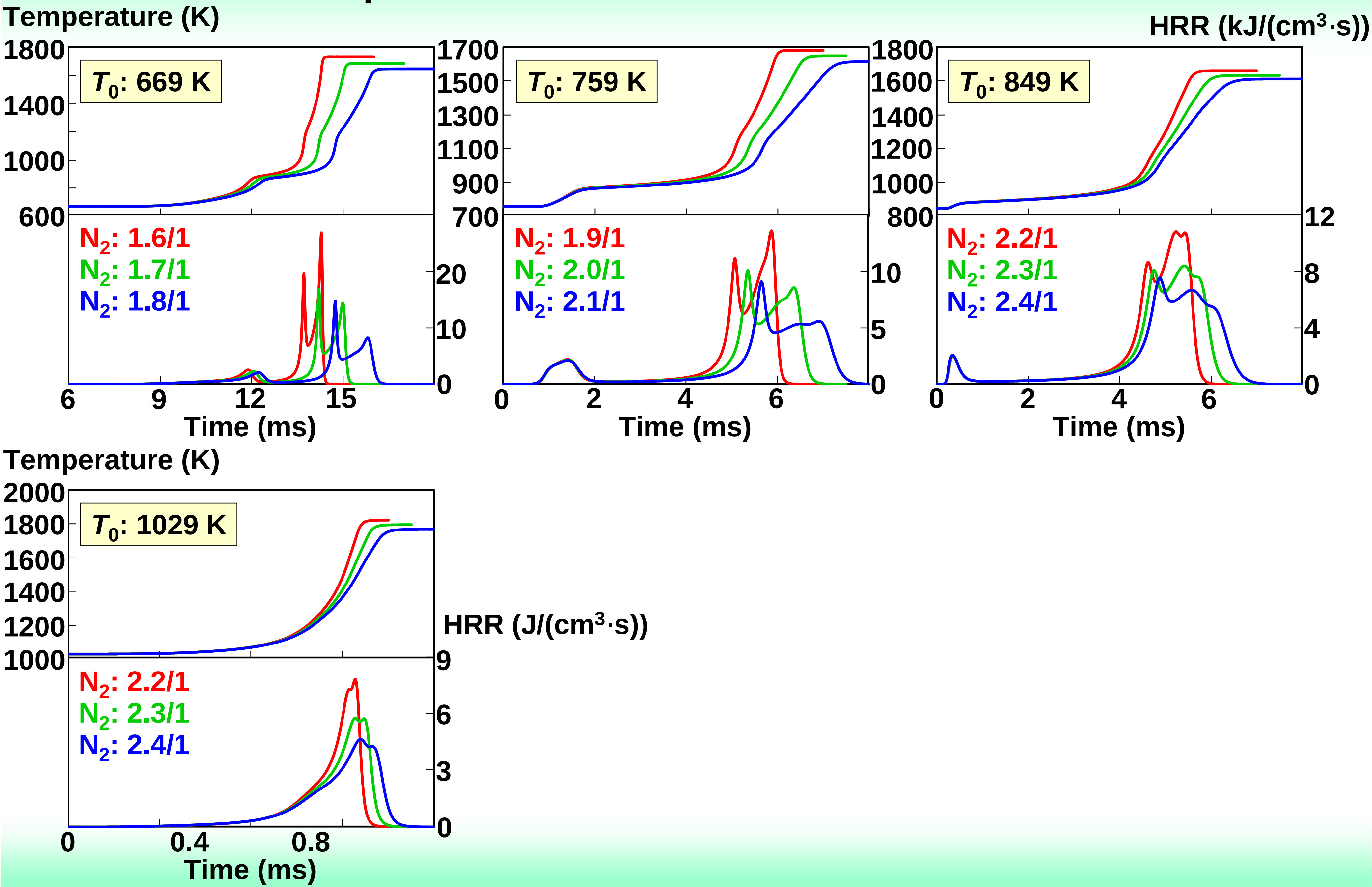

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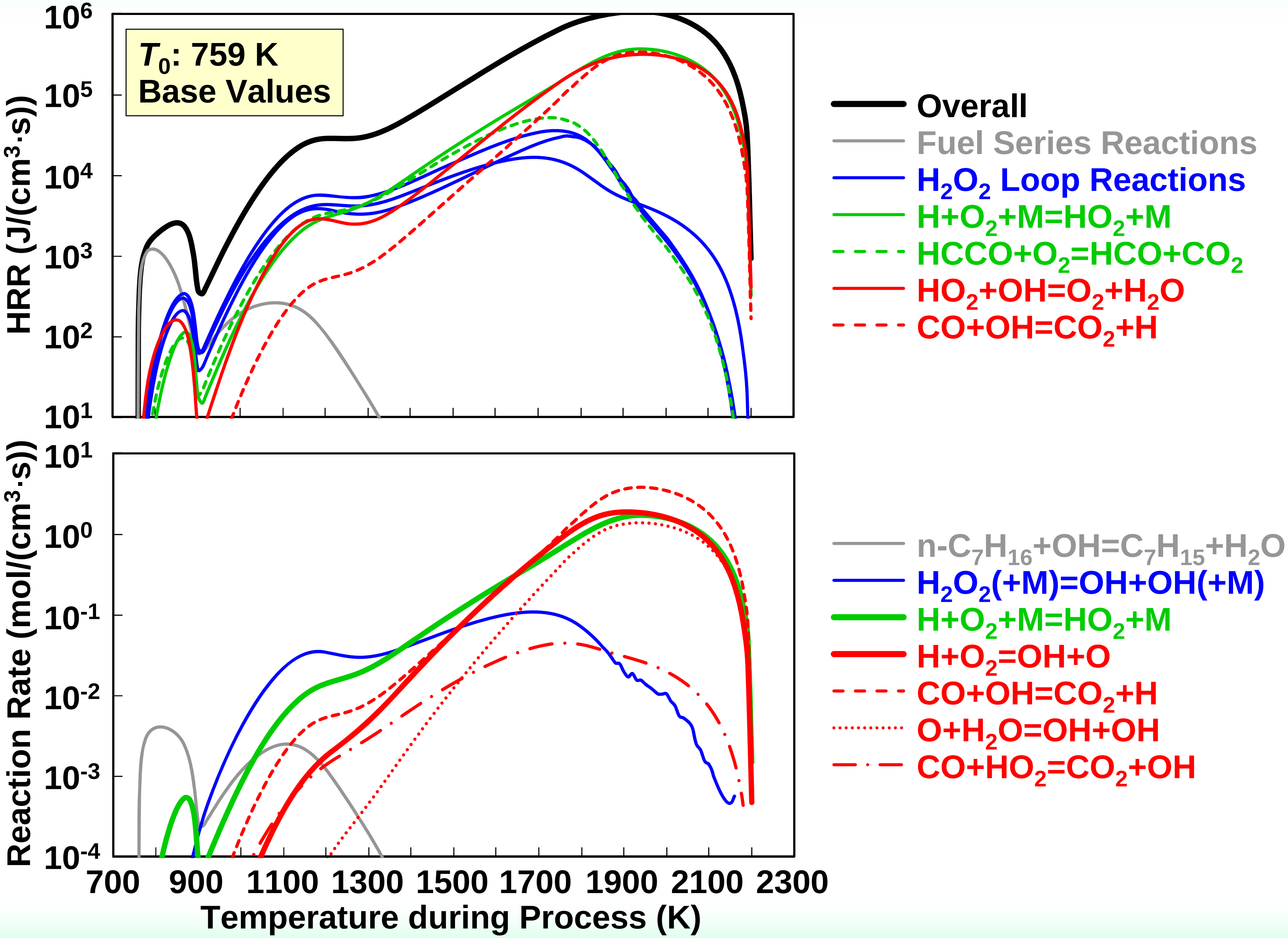
# Heat Release Rates and Reaction Rates with $T_0$: 759 K



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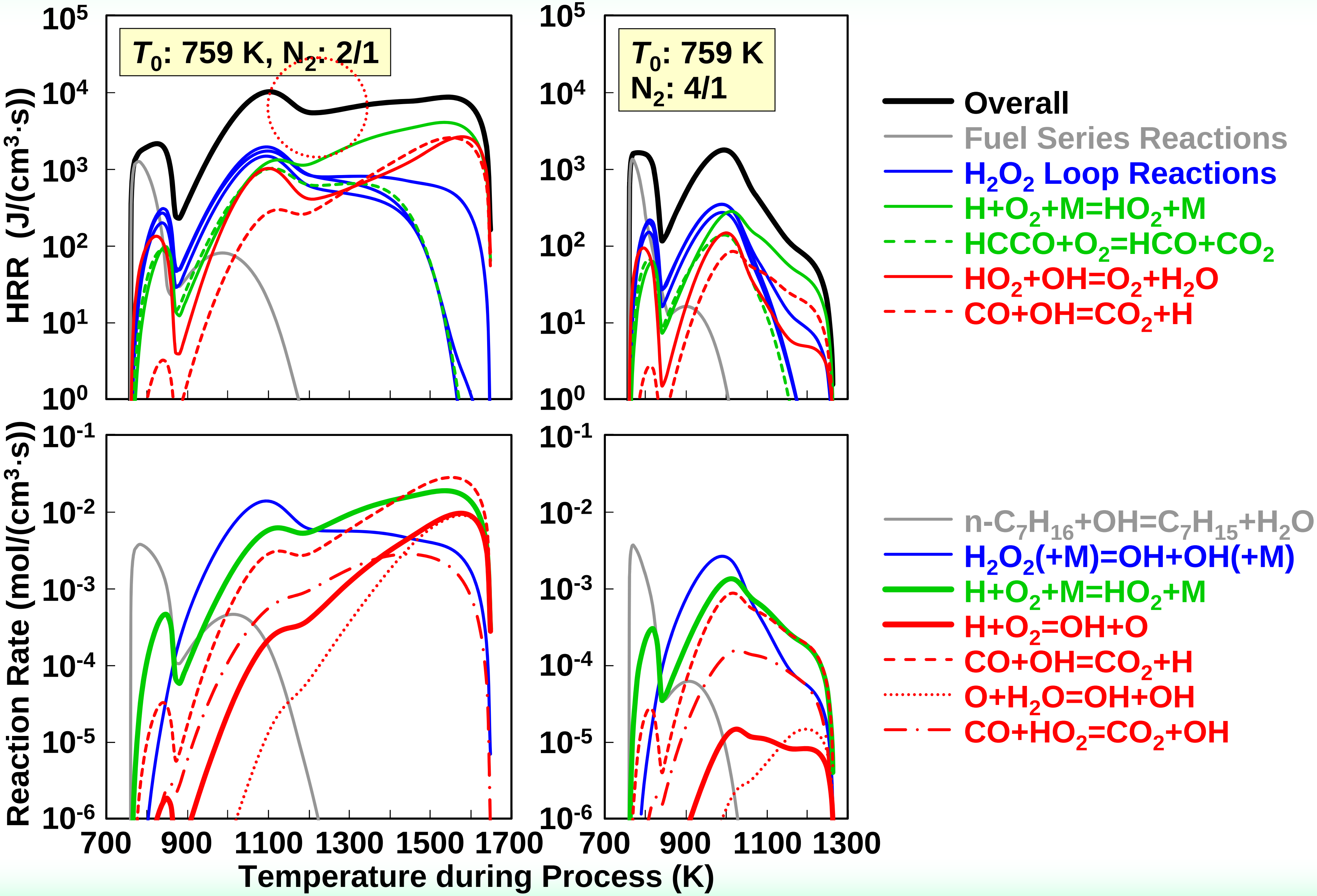
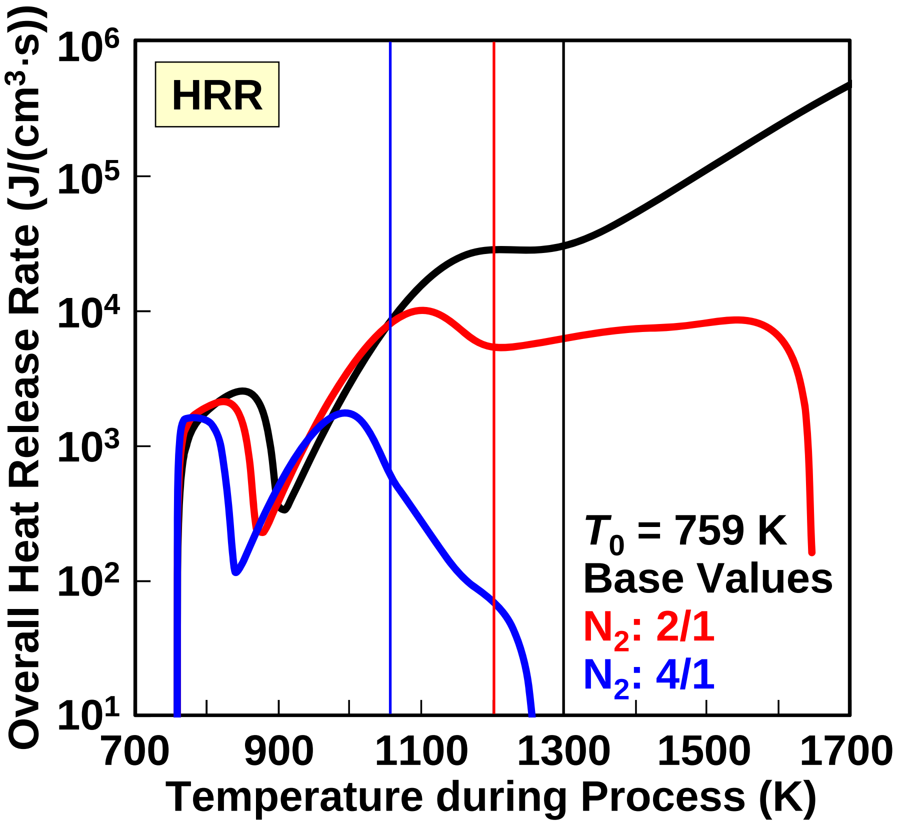
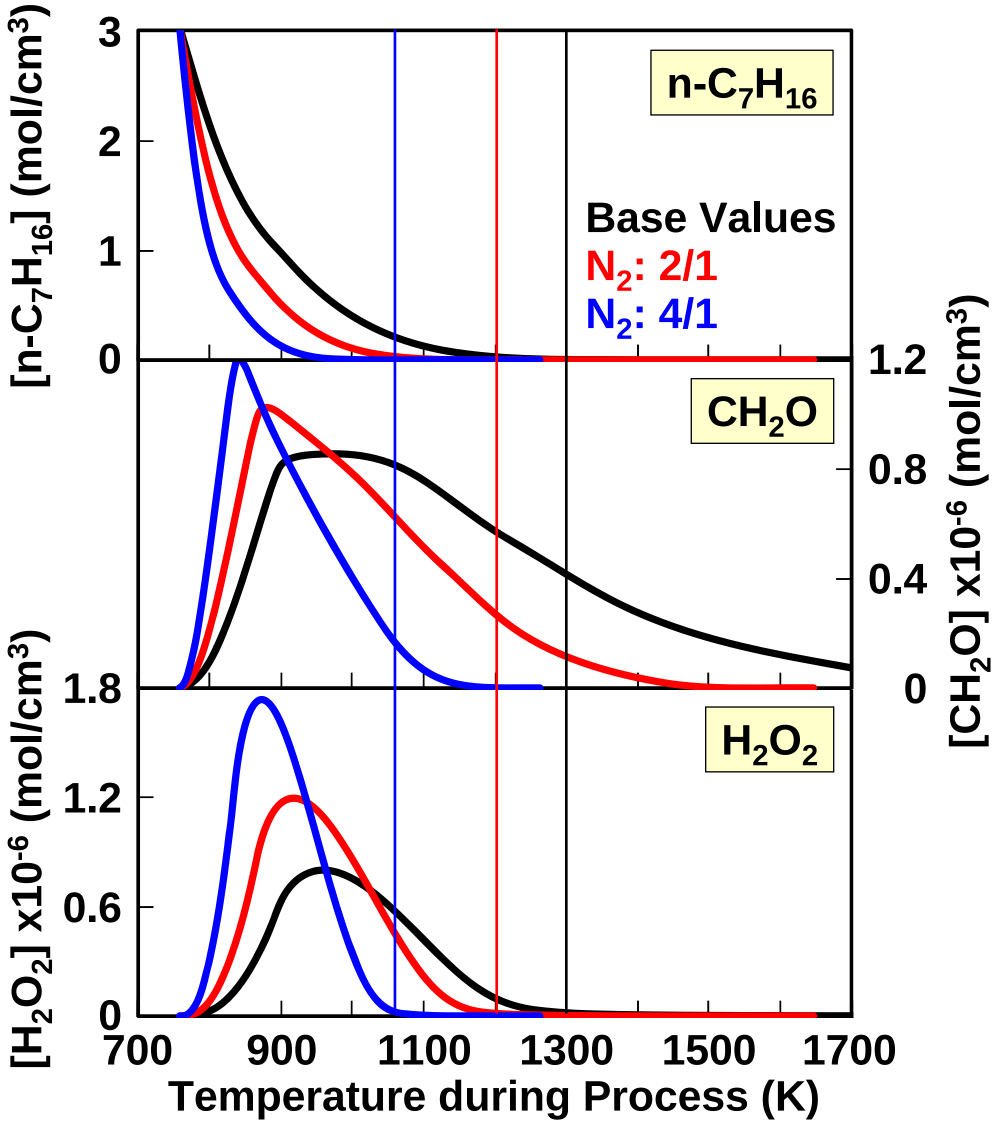


# Fuel, $CH_2O$ and $H_2O_2$ Concentrations with $T_0$: 759 K





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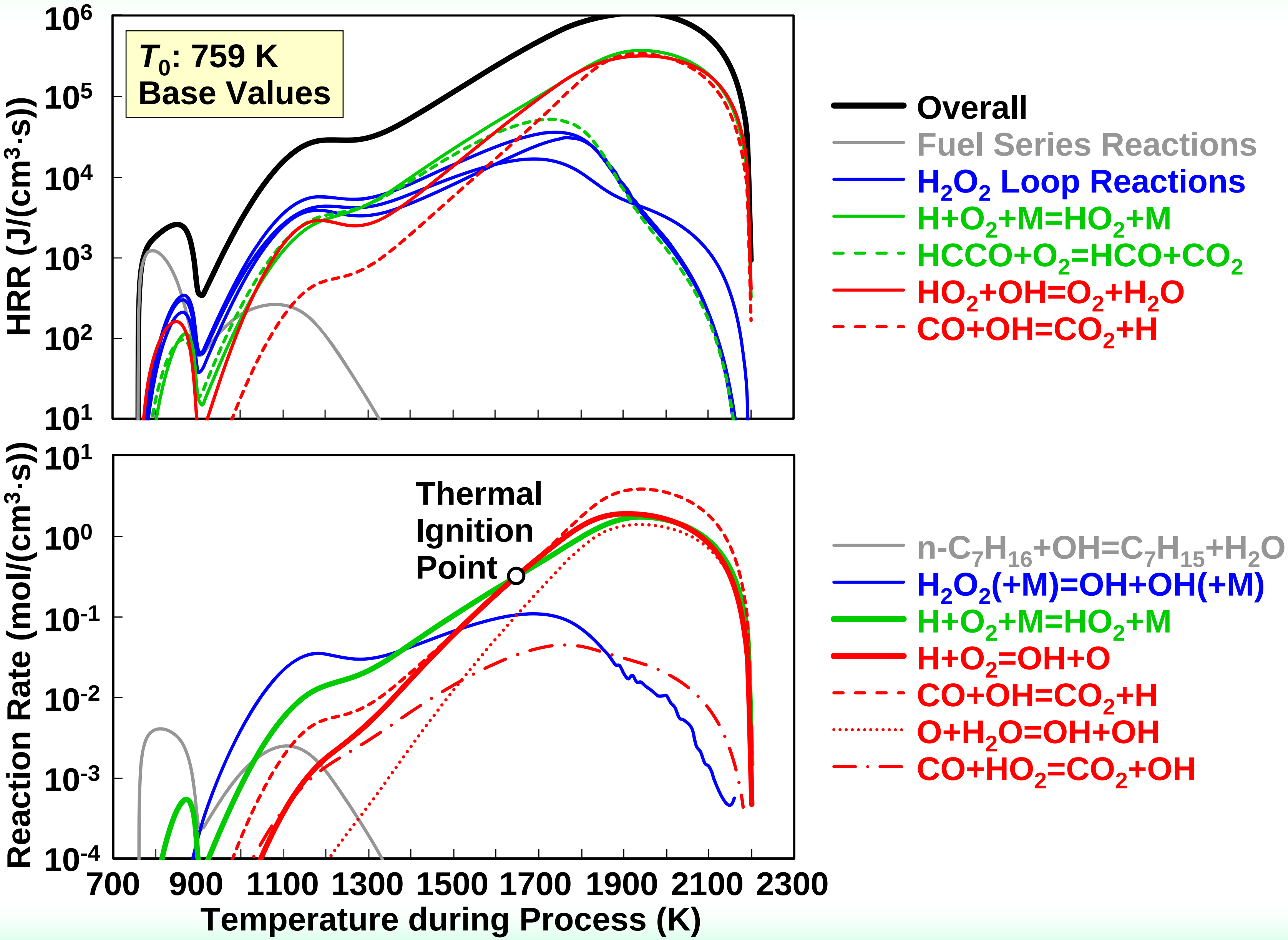

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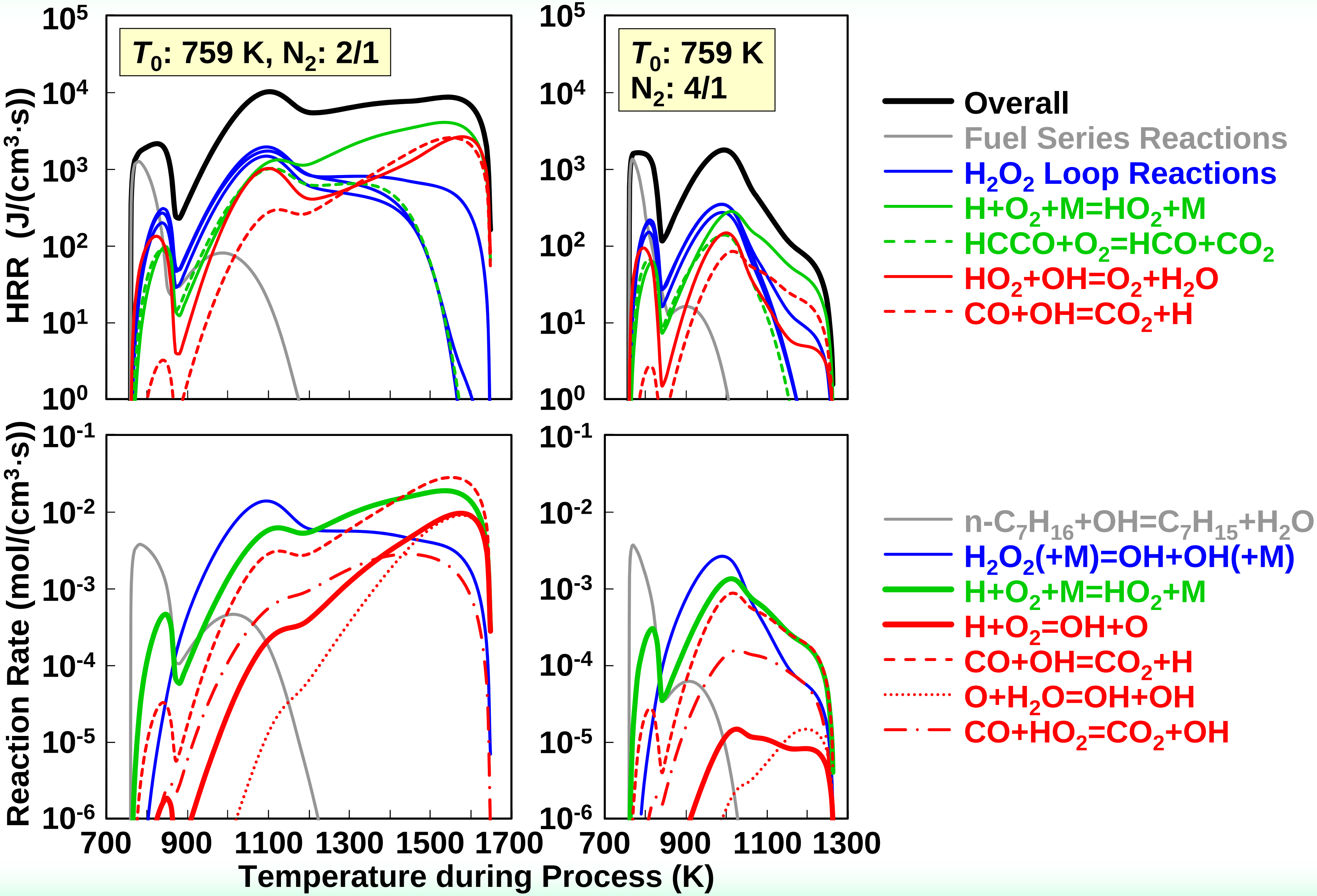
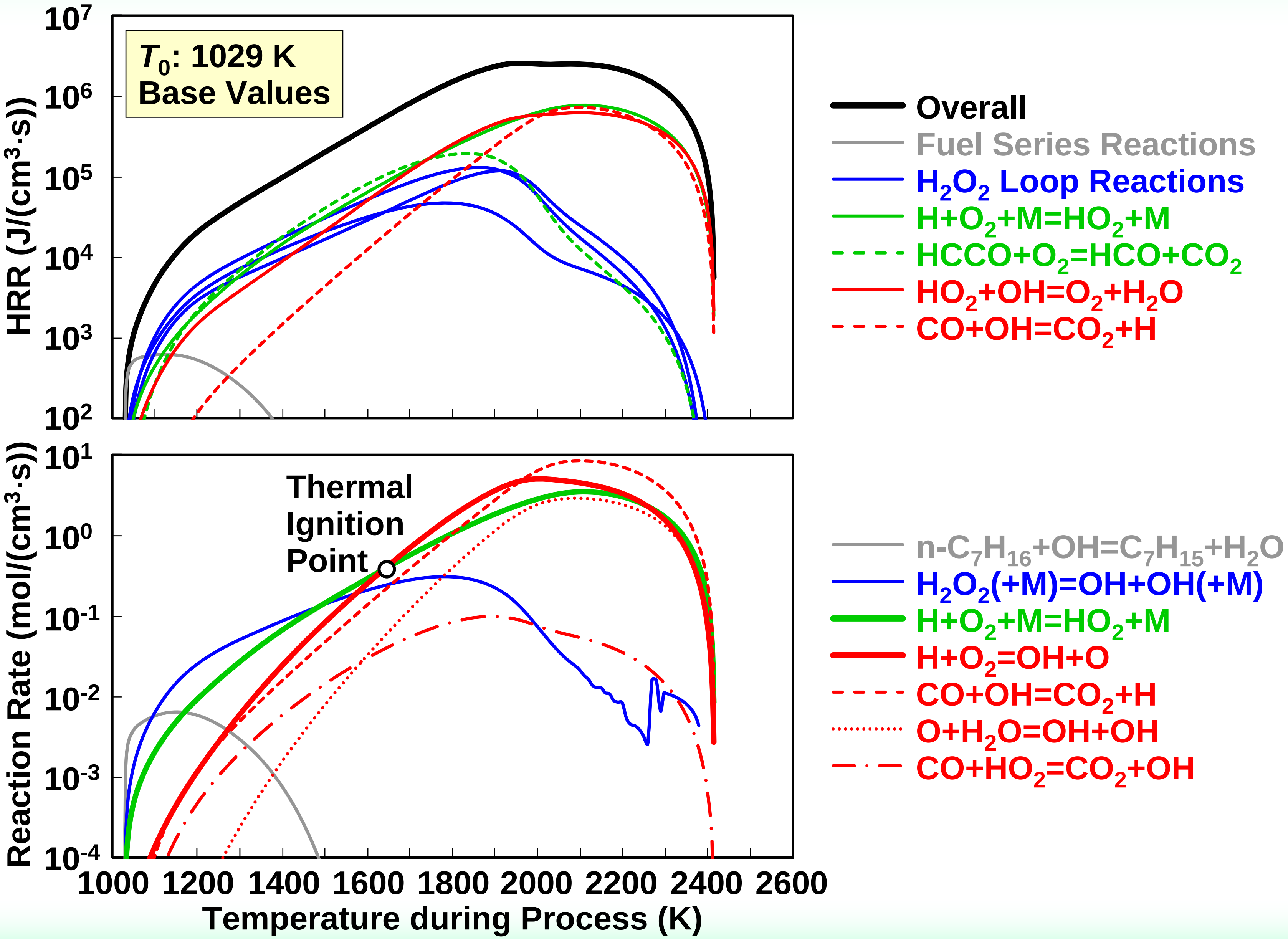


# Heat Release Rates and Reaction Rates with $T_0$: 1029 K



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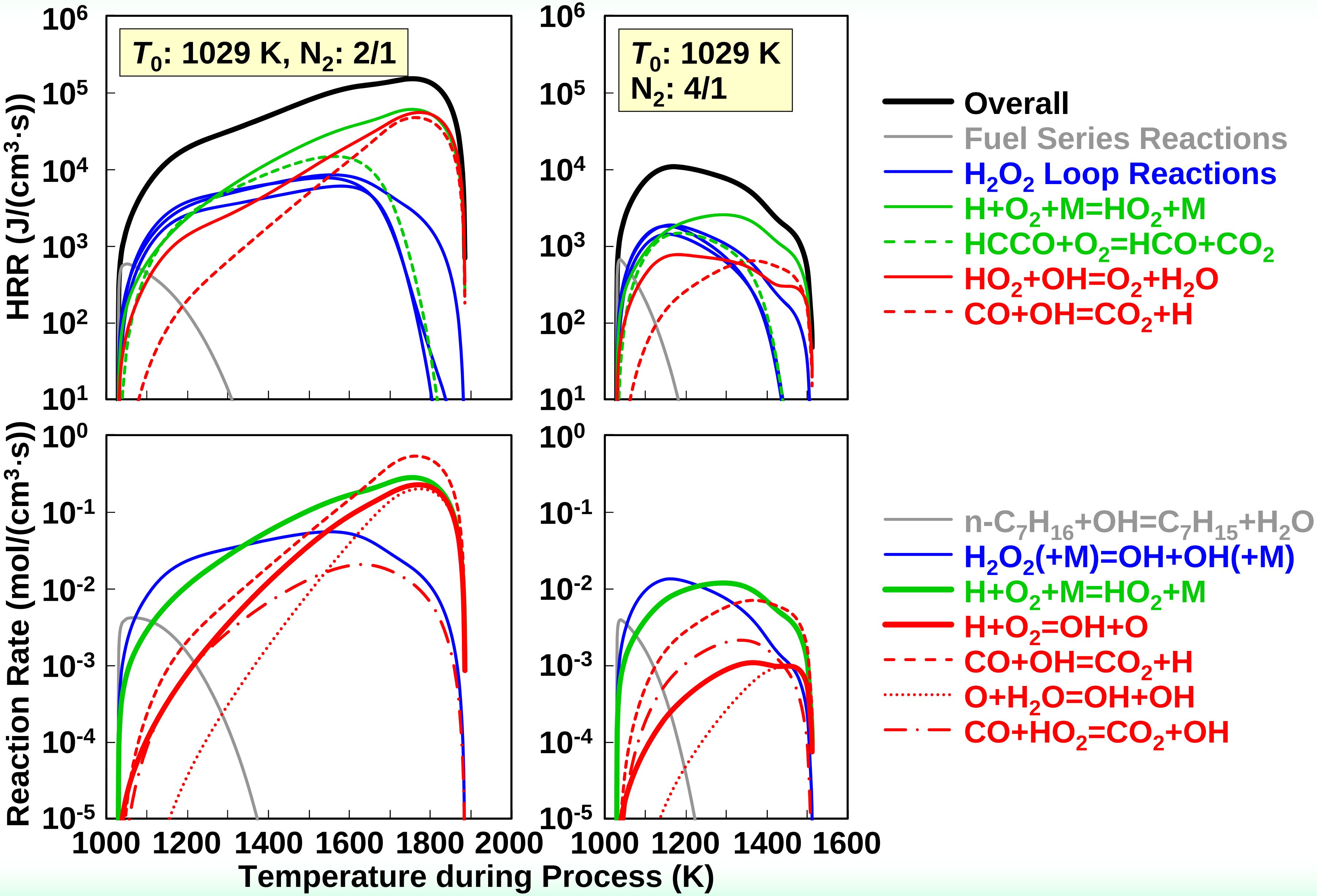

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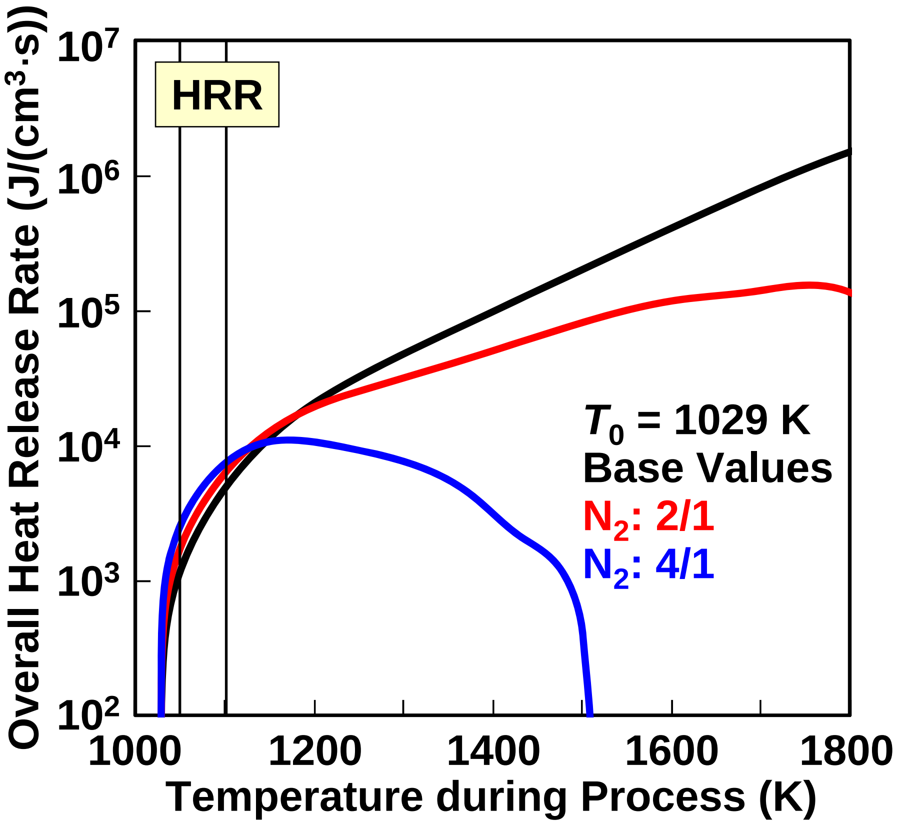


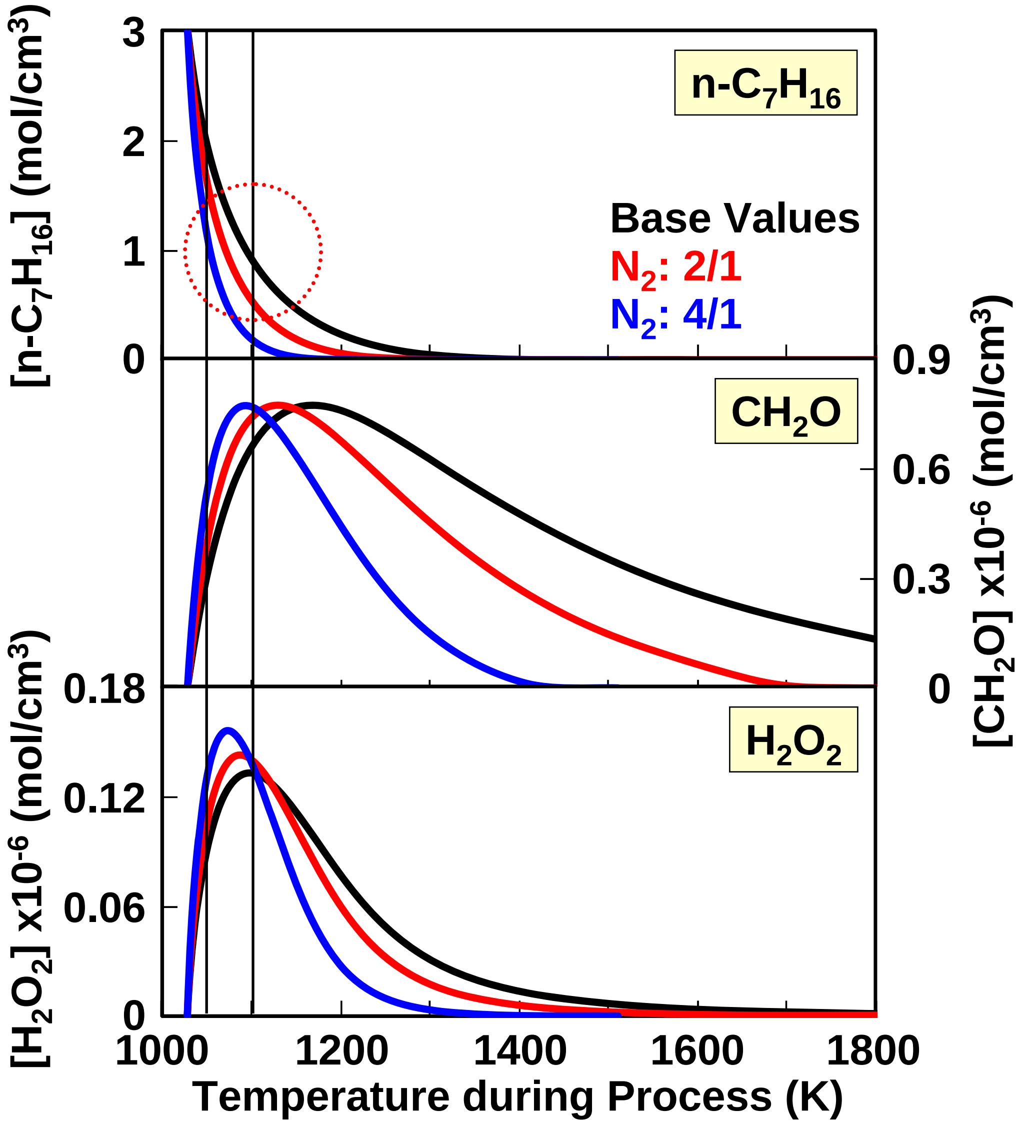

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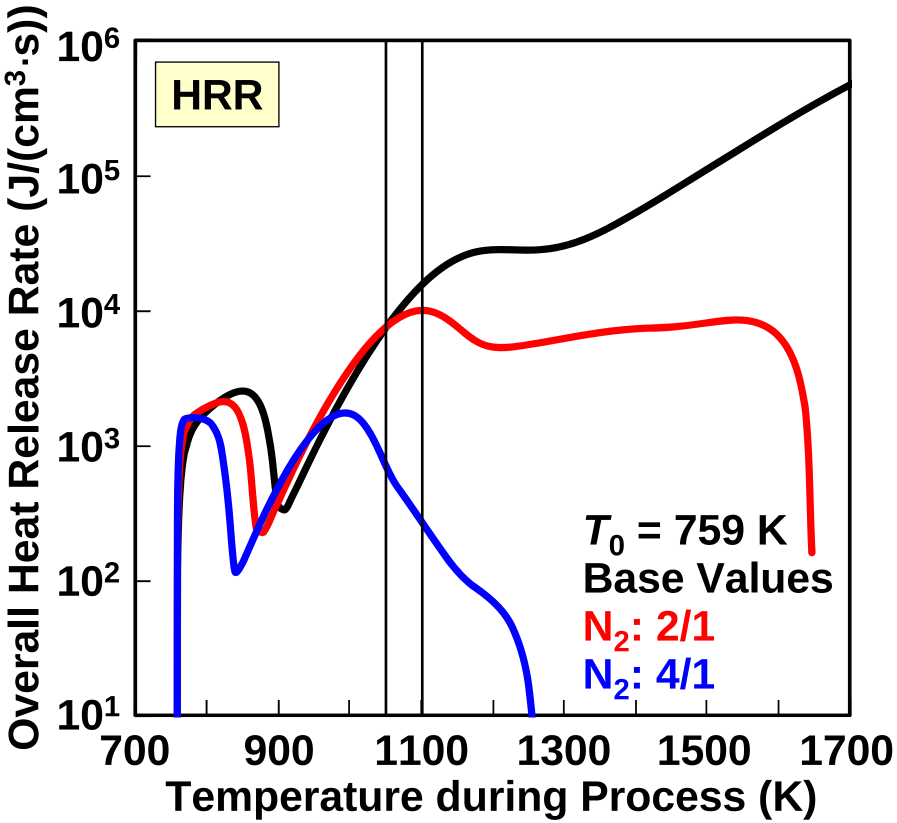
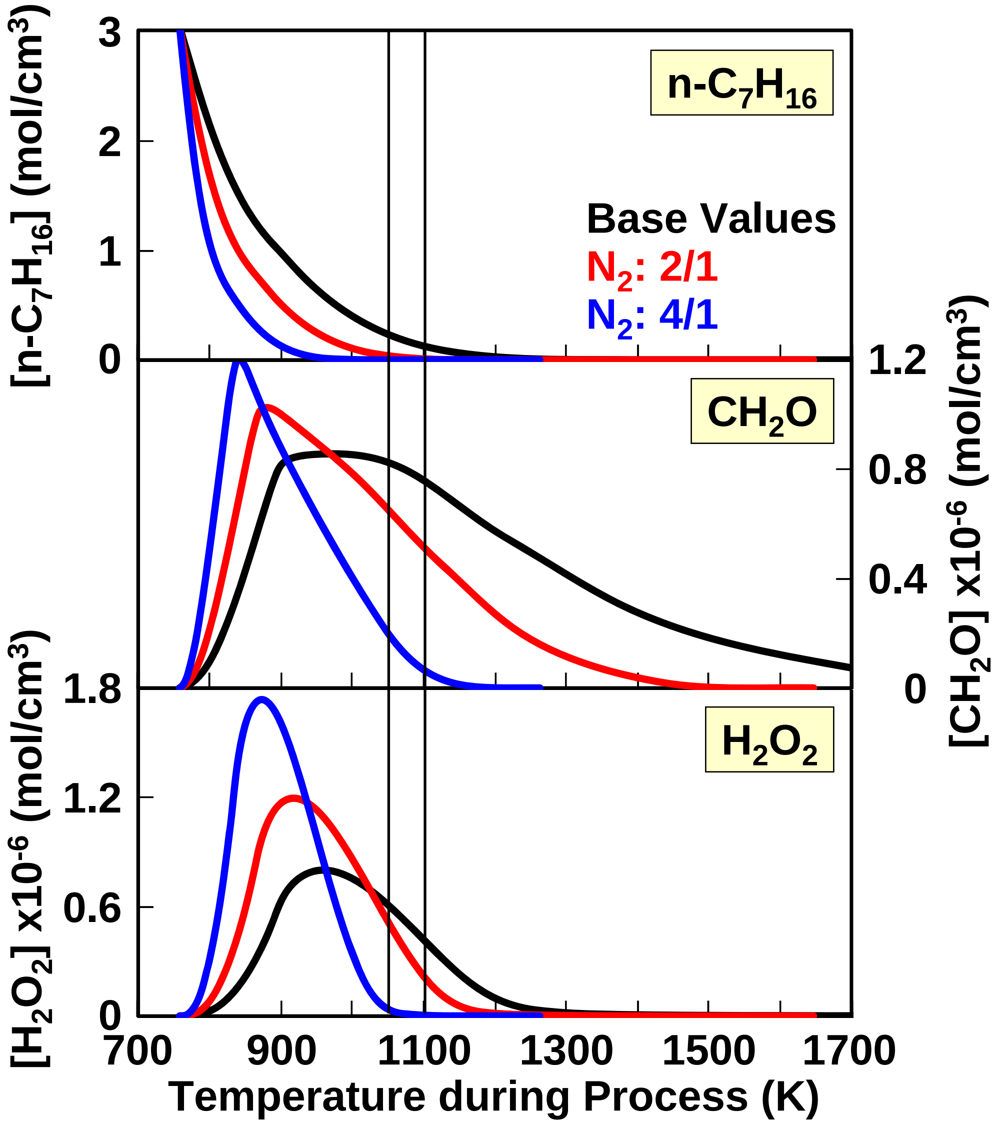
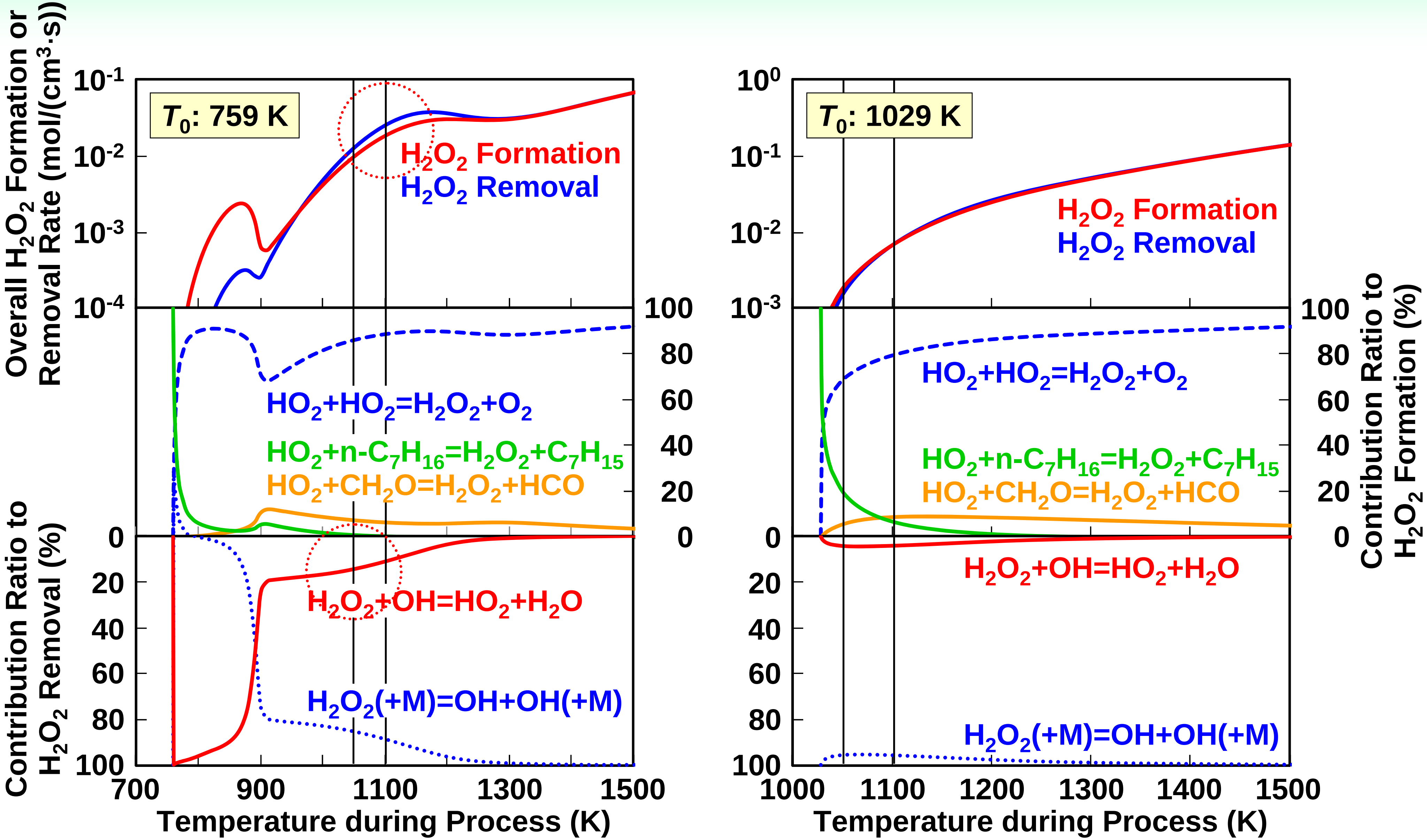


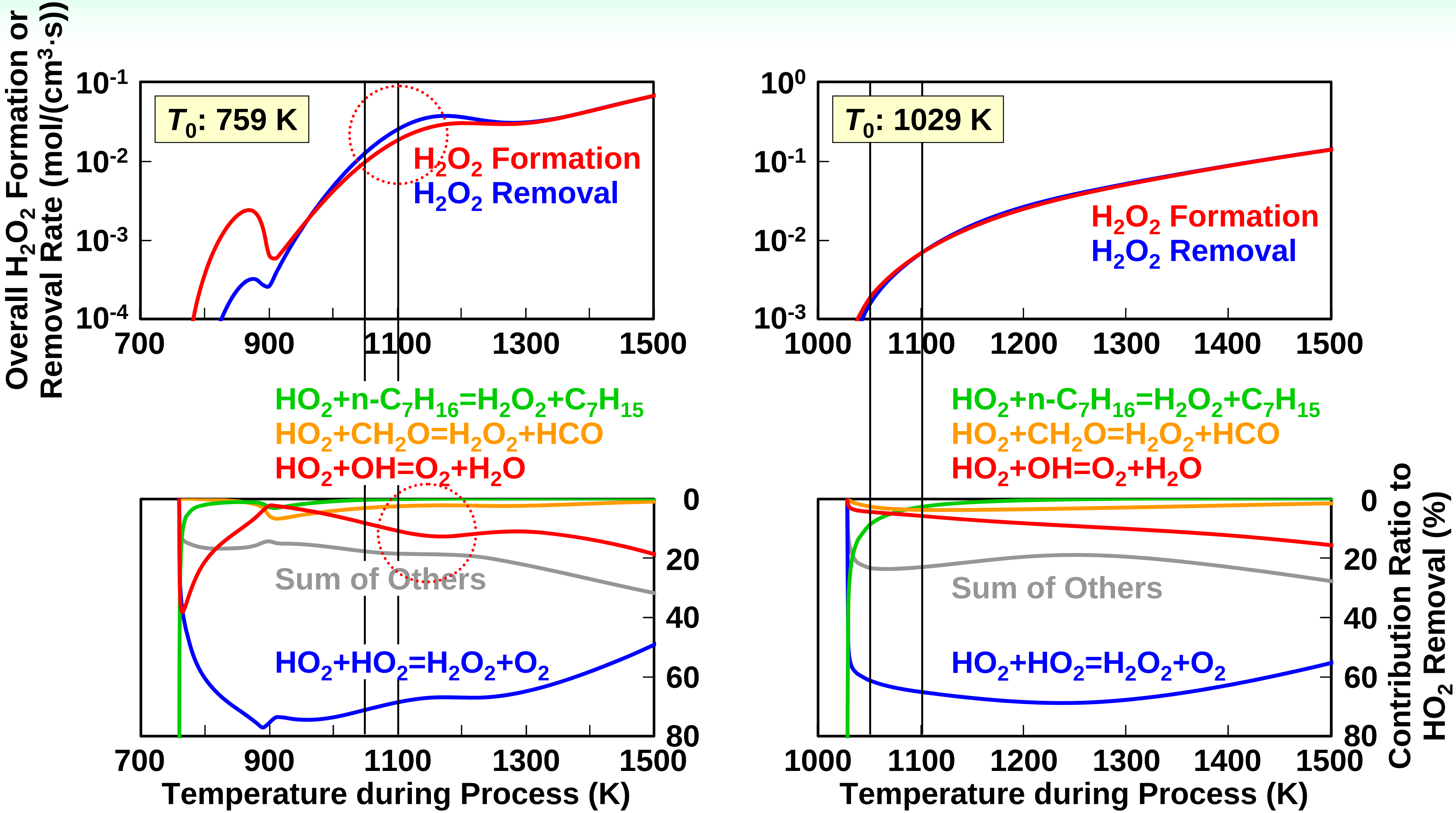
# Contribution Ratios to $H_2O_2$ Formation and Removal





# Contribution Ratios to $HO_2$ Removal





## Summaries

1. When a mixture is highly diluted, an ignition process with LTO indicates two peaks of the heat release in the thermal ignition preparation phase.
   The mechanism of the two-stage heat release is;

2. When the fuel is consumed in the early stage of the thermal ignition preparation phase, n-$C_7H_{16}+HO_2=C_7H_{15}+H_2O_2$ is reduced, and $H_2O_2+OH=HO_2+H_2O$ and $HO_2+OH=O_2+H_2O$ are enhanced.
   Which decreases the efficiency of the $H_2O_2$ regeneration loop, and $H_2O_2$ is consumed in the middle stage of the thermal ignition preparation phase.

3. In the ignition process of highly-diluted mixtures, the rate of $H+O_2=OH+O$ cannot overtake the rate of $H+O_2+M=HO_2+M$.
   $CO+OH=CO_2+H$ proceeds slowly with $H+O_2+M=HO_2+M$, not with the branching chain reaction, in the final stage of the ignition process.

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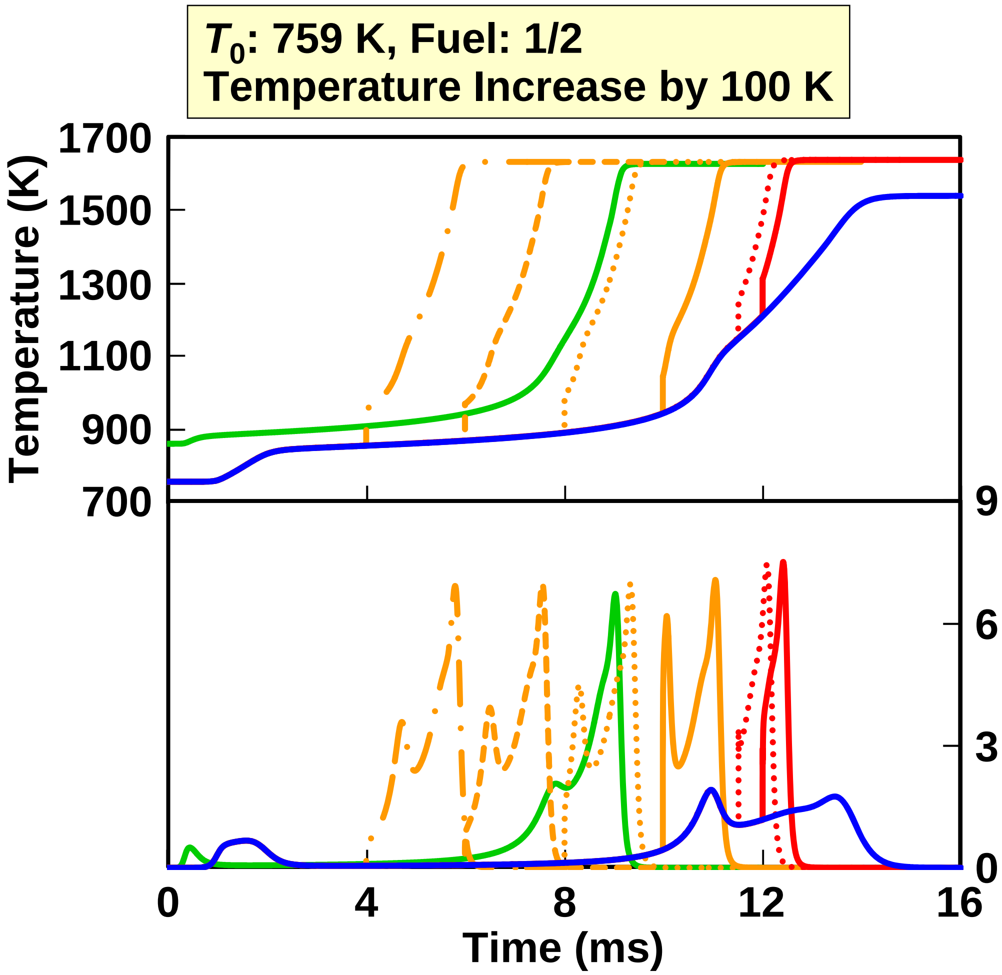
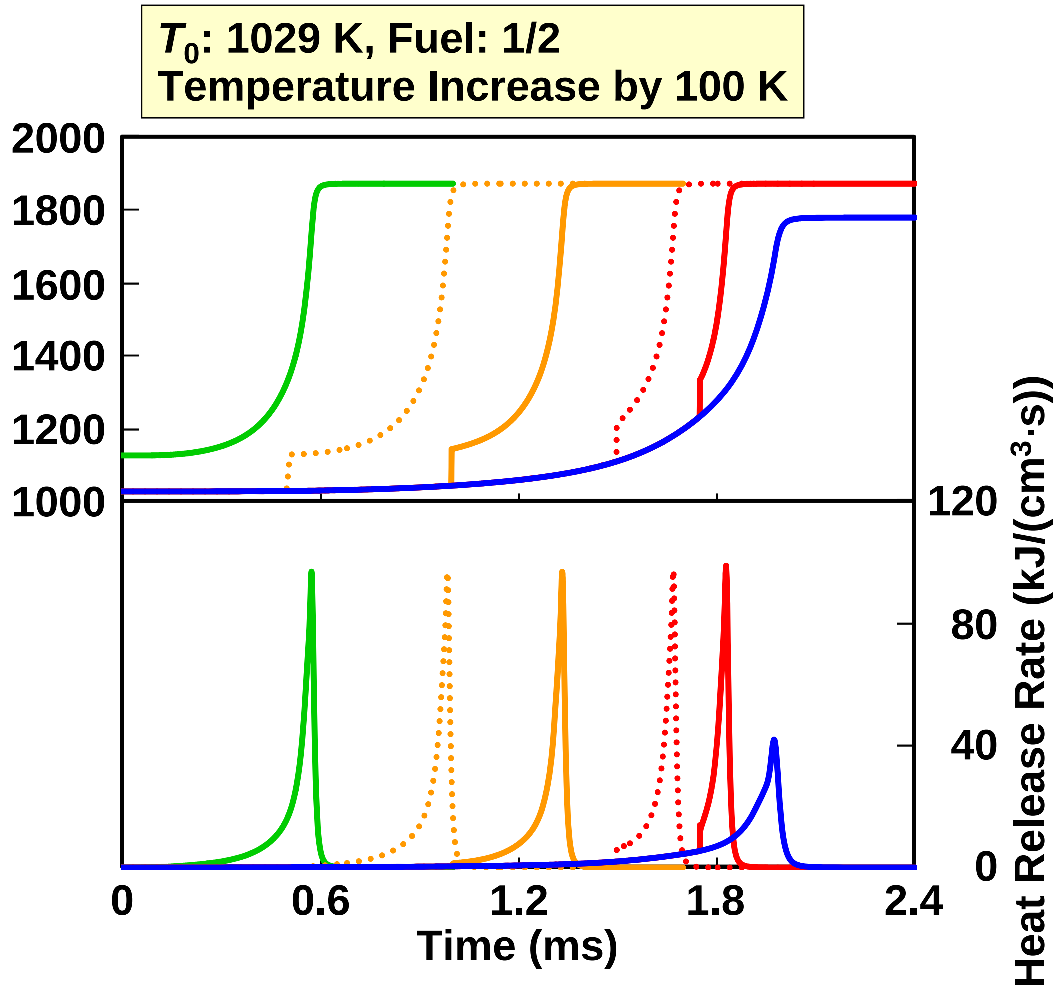
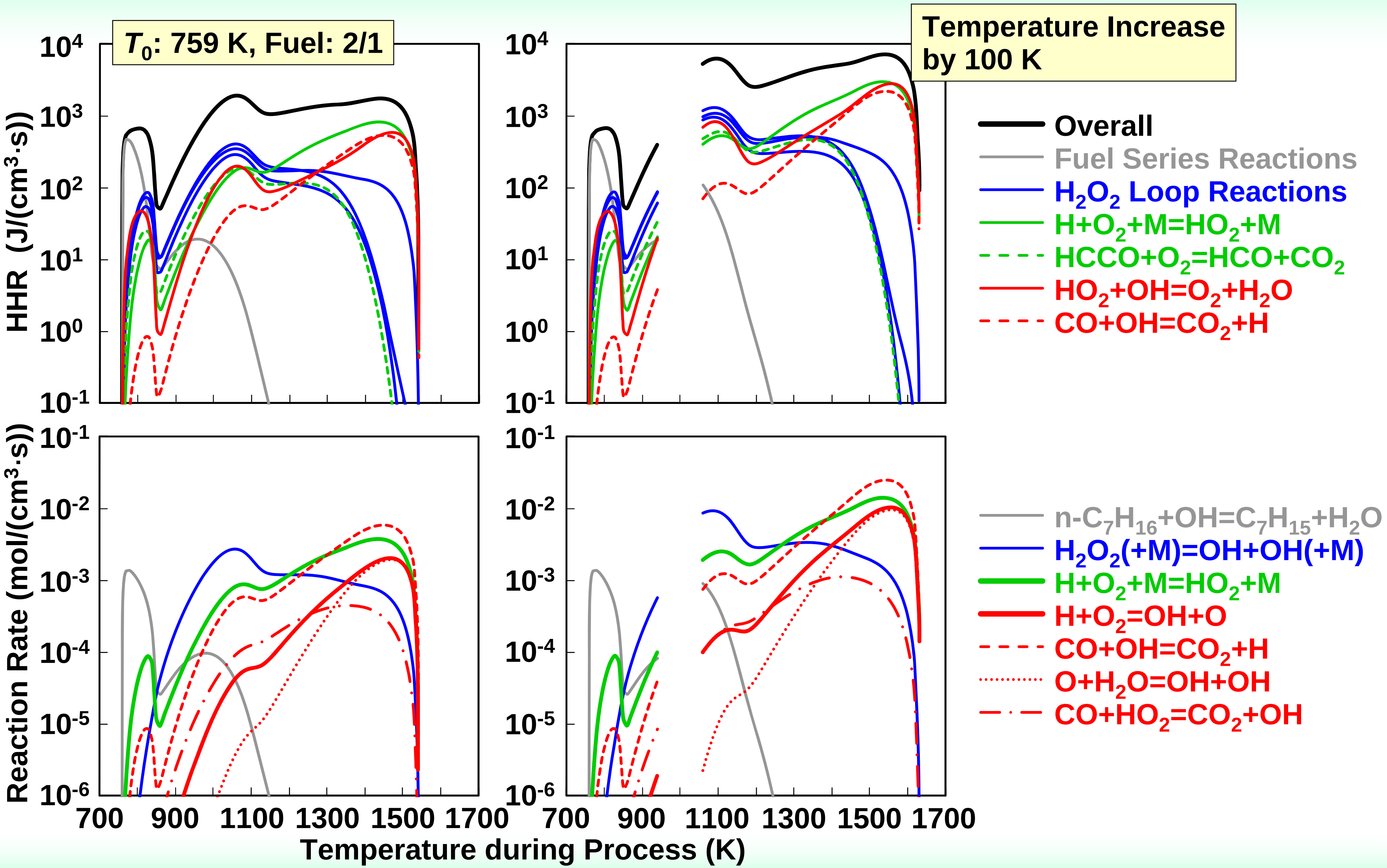
# Activation by Temperature Increase in Ignition Process



# Heat Release Rates and Reaction Rates with $T_0$: 759 K





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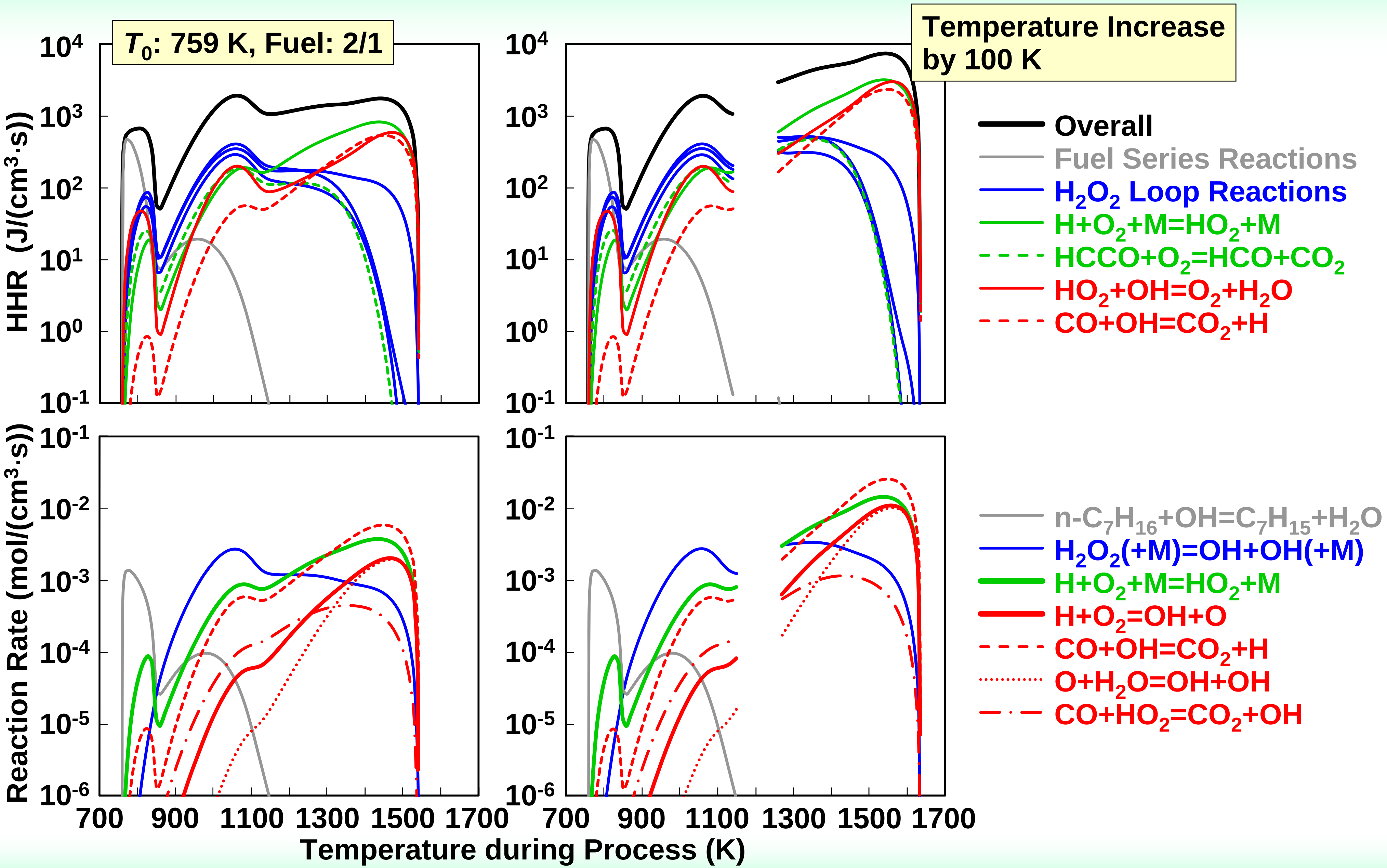
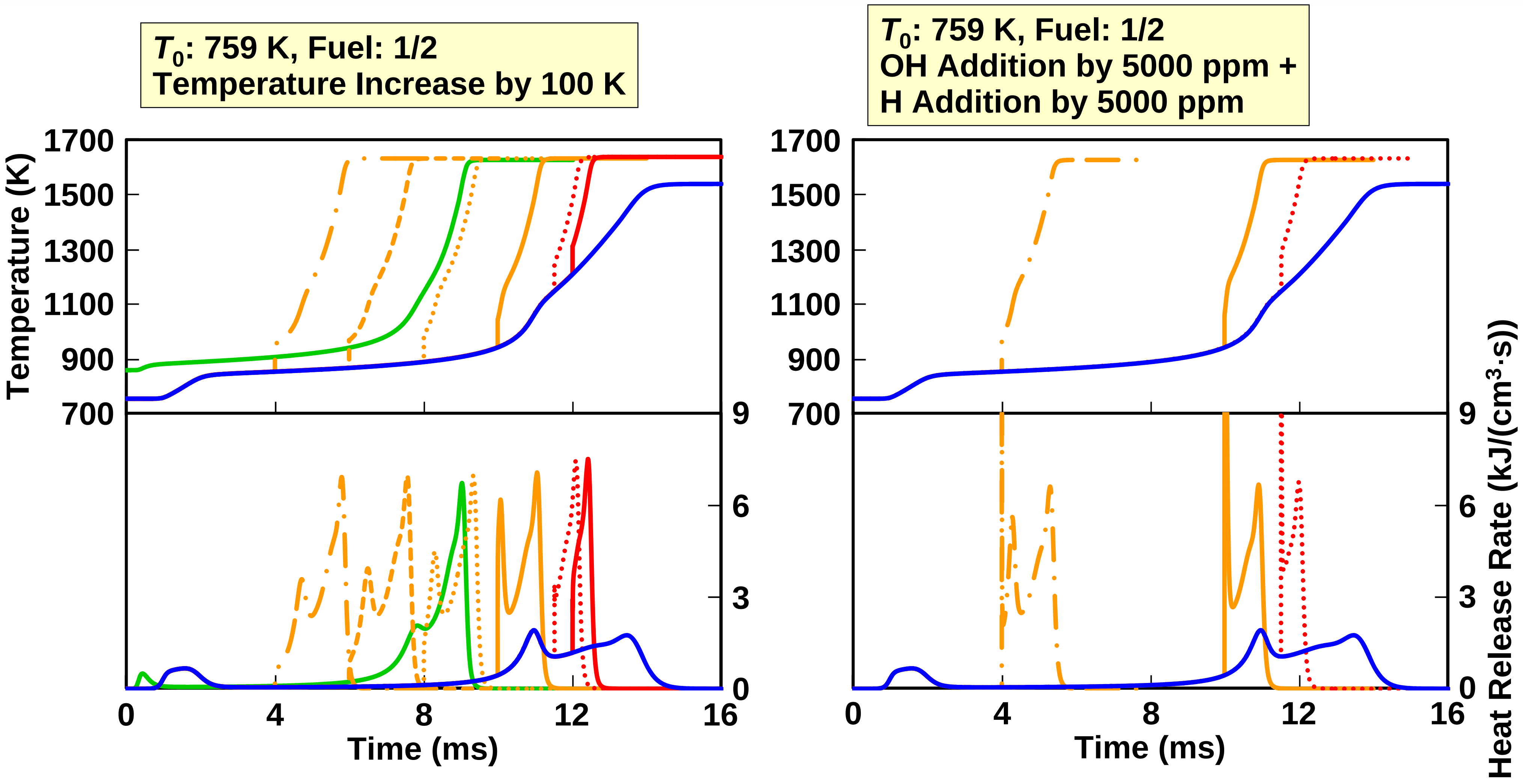


# Activation by OH and H Addition in Ignition Process





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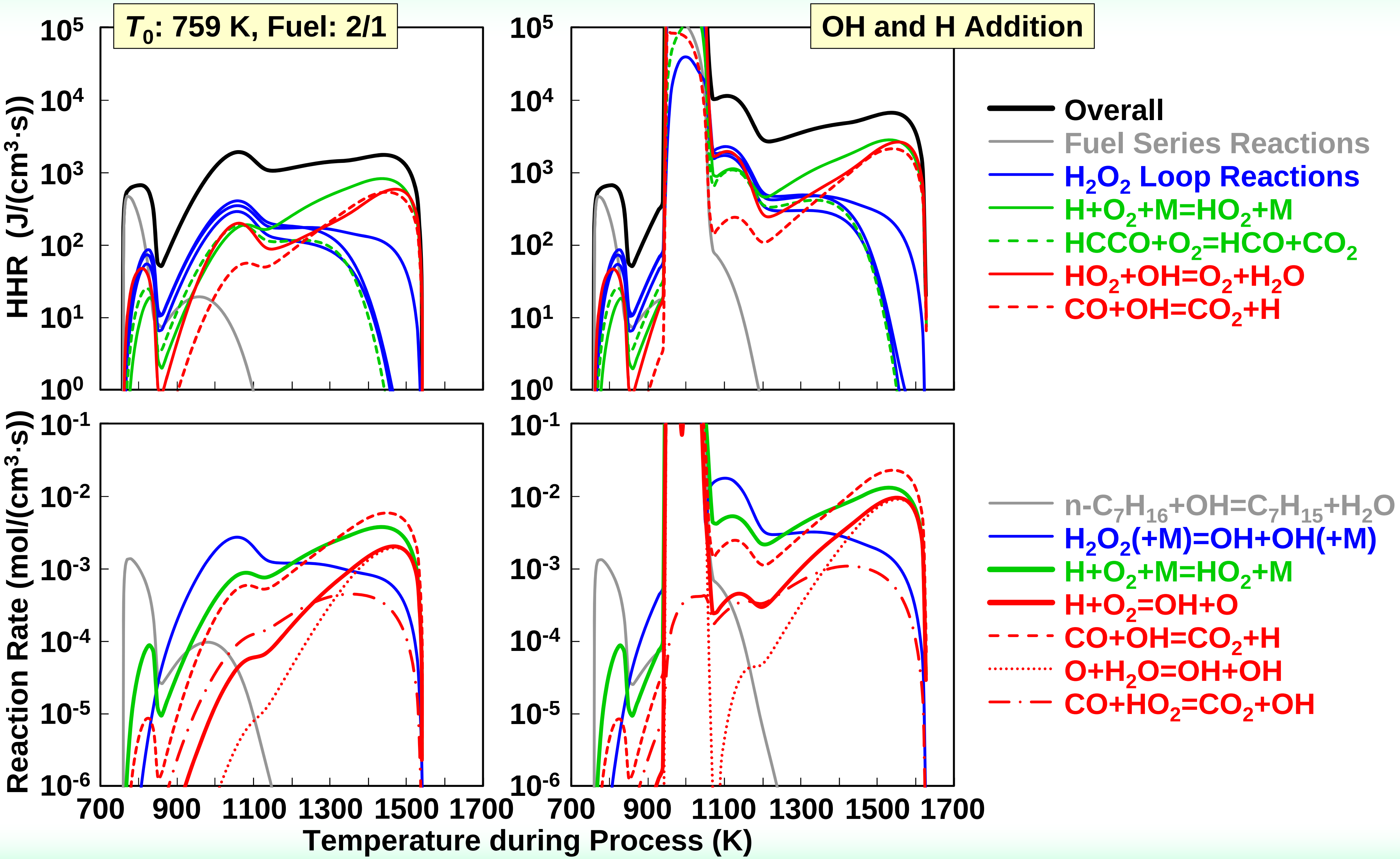

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