

## Introduction

The dynamics of two-stage autoignition of a homogeneous *n*-heptane/air mixture is analyzed algorithmically, using tools of the *Computational Singular Perturbation (CSP)* method. Due to the fast/slow character of this reactive system its dynamics are dominated by the components of the system that generate explosive scales, which tend to lead the system away from equilibrium [1,2]. The reactions that are responsible for the generation of these time scales and the species that relate with these scales are identified with CSP-tools.

## The Physical Problem

We consider adiabatic autoignition at constant volume of a homogeneous stoichiometric *n*-heptane/air mixture. The governing equations for the species mass fraction and temperature are:

$$\frac{dy}{dt} = \frac{1}{\rho} \mathbf{W} \cdot \sum_{k=1}^{2K} \mathbf{S}_k R^k \quad (1)$$

$$\frac{dT}{dt} = \frac{1}{\rho c_v} (-\mathbf{h}_c \cdot \mathbf{W} + RTU) \cdot \sum_{k=1}^{2K} \mathbf{S}_k R^k \quad (2)$$

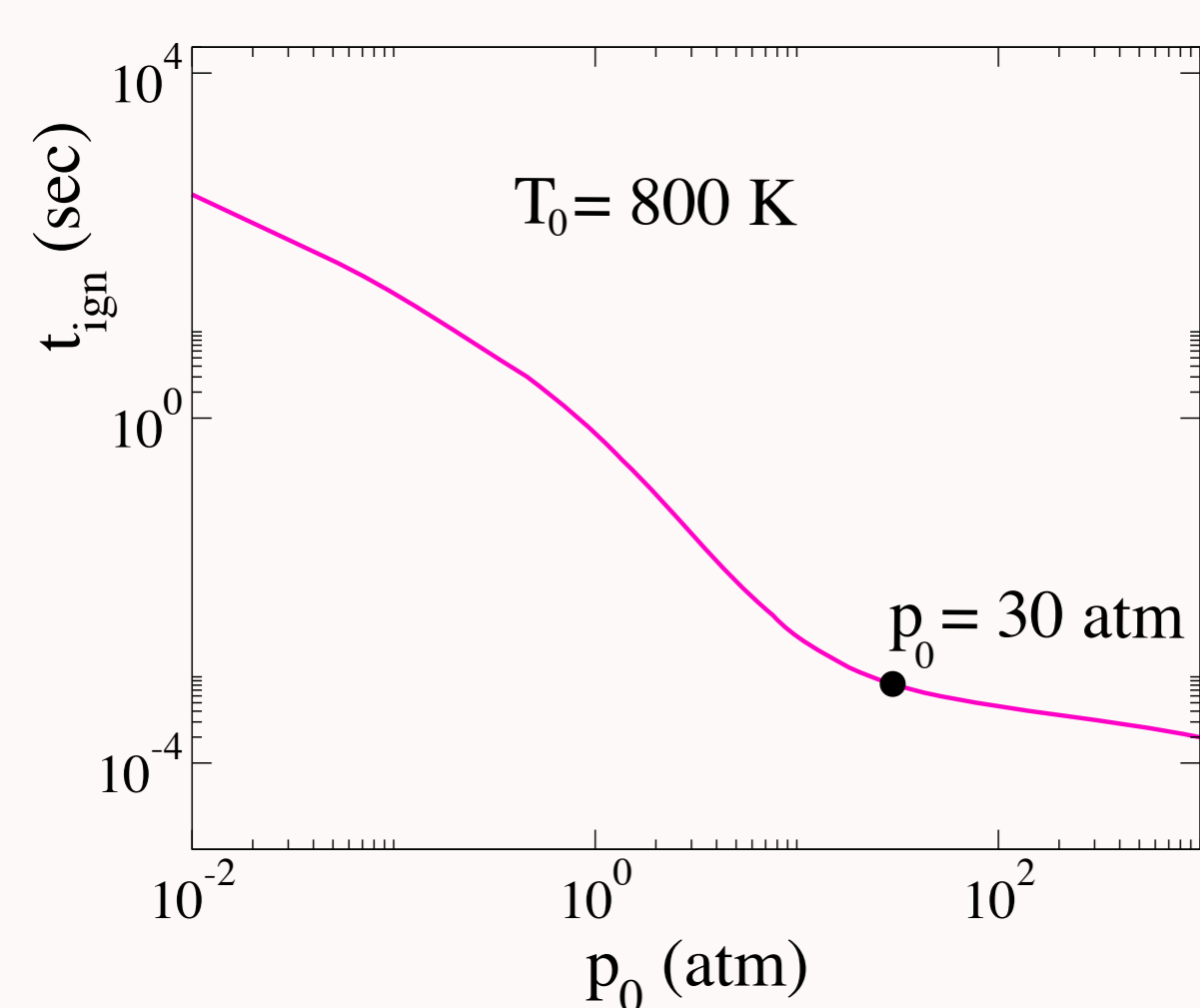


Figure 1: Ignition delay time as a function of  $p_o$  at  $T_o = 800$  K. The black bullet indicates the case that will be analyzed.

The ignition delays for a wide range of initial pressures  $p_o$  at  $T_o=800$ K are shown in Fig 1. The two-stage autoignition occurs in the range of 1 – 100 atm. An extensive analysis of the dynamics of the two-stage ignition of *n*-heptane for skeletal mechanisms in this region was conducted by Peters et al. [3].

A detailed analysis will be performed for the case of  $p_o = 30$  atm and  $T_o =$

800 K. CSP tools will be employed in order to identify the reactions that generate the explosive time scale  $\tau_{e,f}$ , the magnitude of which approximates  $t_{ign}$ ; i.e.  $t_{ign} = O(\tau_{e,f})$  [4]. An elementary study of the influence of the fast explosive time scale for the two-stage ignition of *n*-heptane was conducted by Diamantis et al. [5].

## Autoignition Dynamics of *n*-heptane/air Mixture

Shown in Fig. 2 are the explosive timescales,  $\tau_e$ 's, that develop during the autoignition of a stoichiometric *n*-heptane/air mixture in the case  $T_o = 800$  K,  $p_o = 30$  atm, along with the temperature profile.

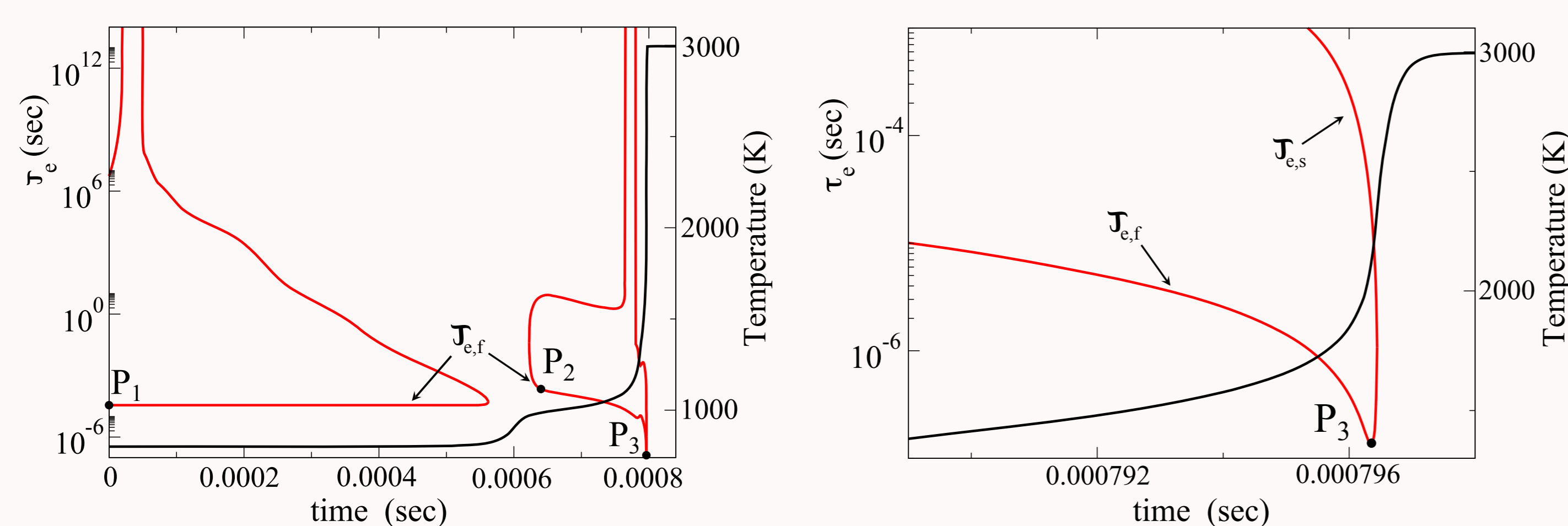


Figure 2: The evolution of the developing explosive timescales,  $\tau_e$ , (red line) and temperature (black line) as a function of time:  $P_o = 30$  atm,  $T_o = 800$  K and  $\phi = 1$ .

The reactions that generate  $\tau_{e,f}$  and the variables that are most related to  $\tau_{e,f}$  will be identified at three points:

- $P_1$ : the initiation of the process
- $P_2$ : right after the *first stage*
- $P_3$ : right before the *explosive stage*, where  $\tau_{e,f}$  gets minimum

as shown in Fig. 2.

The CSP tools that will be employed are the *Time Scale Participation Index (TPI)* and the *CSP Pointer*; the first measures the relative contribution of each reaction to  $\tau_{e,f}$ , while the second measures the relation of each variable to  $\tau_{e,f}$ .

## Analysis of the Fast Explosive Mode

Values of TPI and Pointer are reported next at the three points during the autoignition process, as indicated by solid black bullets in Fig. 2.

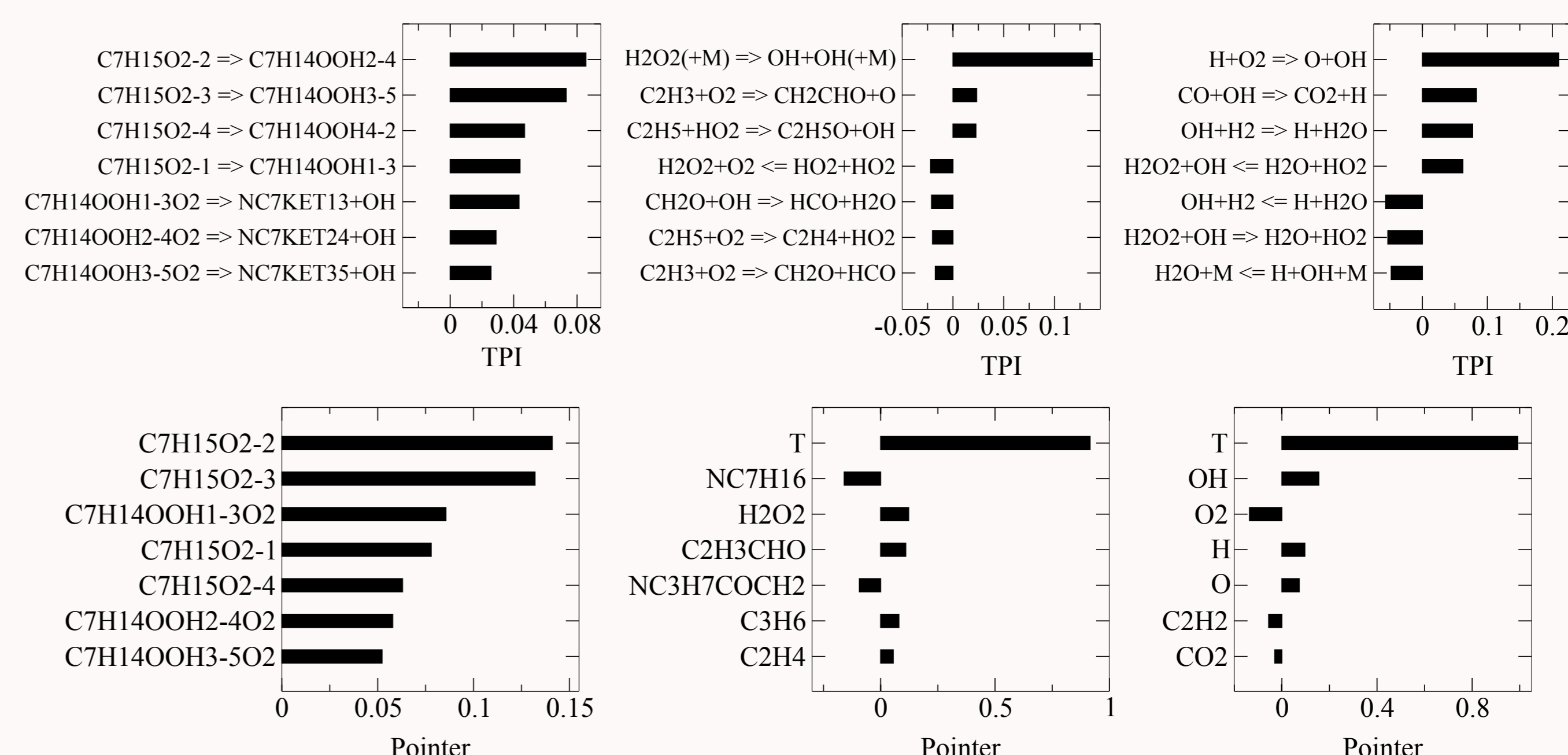


Figure 3: Top: the reactions with the largest Time scale Participation Indices (TPI). Bottom: the species with the largest CSP Pointers at the three selected points.

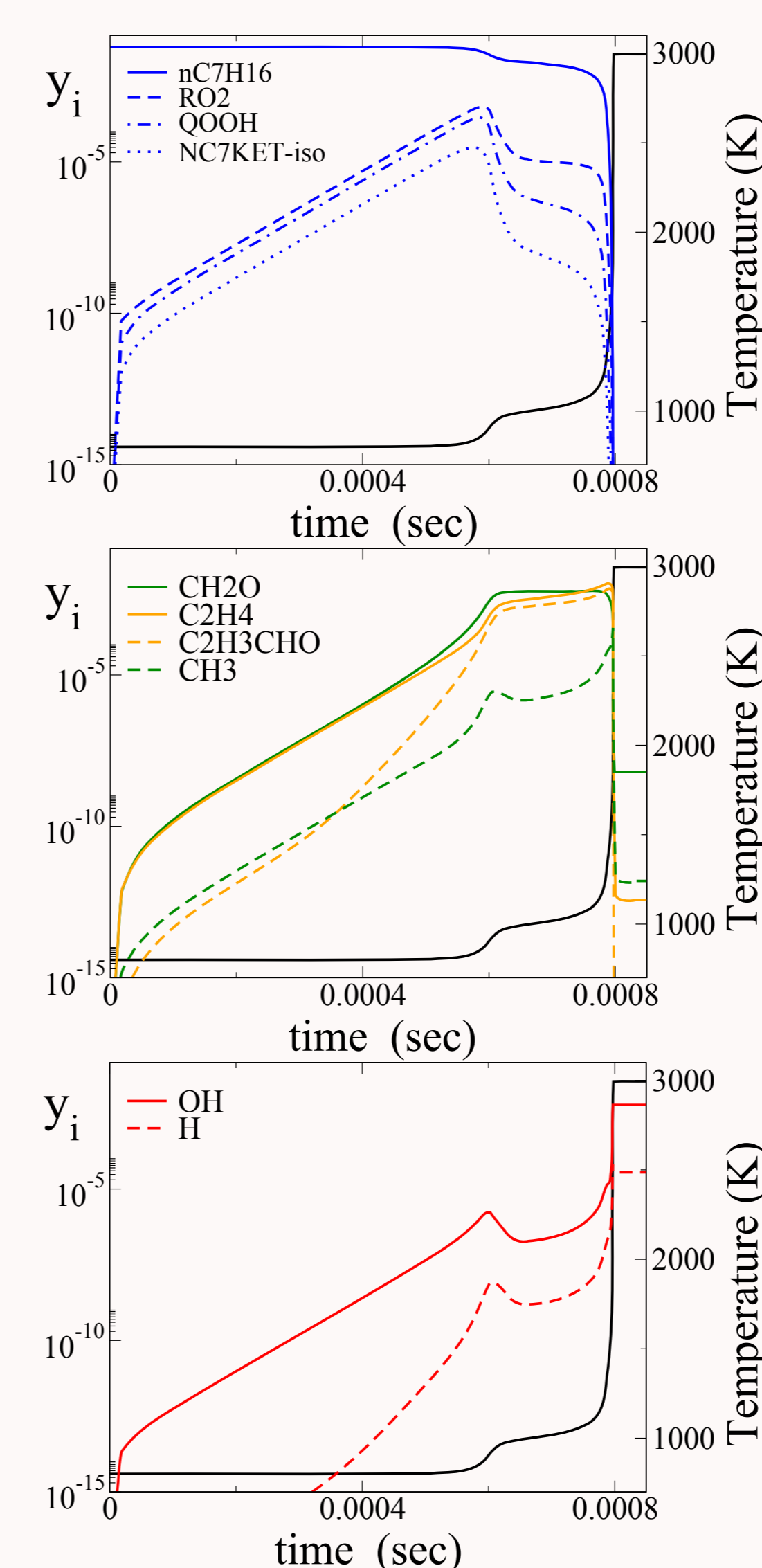


Figure 4: The evolution with time of the temperature and of selected species' mass fraction during the homogeneous autoignition process. The groups of species' mass fractions were selected according to the TPI and Pointer results and represent all the stages of the process.  $p_o = 30$  atm,  $T_o = 800$  K and  $\phi = 1$ .

At  $t = 0$  ( $P_1$ ), it is shown that the major contributors to the generation of  $\tau_{e,f}$  are:

- intramolecular isomerization reactions of  $RO_2$  to  $QOOH$  and
- reactions of peroxyalkylhydroperoxides ( $QOOH - O_2$ ) forming ketohyperoxides and OH

(R:  $C_nH_{2n+1}$  and Q:  $C_nH_{2n}$  groups).

The reactions that oppose the generation of  $\tau_{e,f}$  at  $t = 0$  are dissociation reactions of  $RO_2$  that lead to the formation of Q and  $HO_2$ .

When  $\tau_{e,f}$  re-appears (right before  $P_2$ ), it is generated mainly by the chain branching reaction  $H_2O_2(+M) \rightarrow OH + OH(+M)$ . Since at point  $P_2$  the temperature has already risen around 200 K and keeps rising, it can be concluded that this point lies in the *thermal runaway regime*, in agreement with the Pointer which identifies the temperature as the variable related the most to  $\tau_{e,f}$ .

In the vicinity of point  $P_3$ , the highly exothermic  $H_2/O_2$ -chemistry is dominating the generation of  $\tau_{e,f}$ .

## Conclusions

- As the process evolves, the nature of the reactions related to the characteristic explosive time scale evolves as well.
- In the period that leads to the first stage, the reactions promoting  $\tau_{e,f}$  are heptane isomerization reactions, such as intramolecular isomerization reactions of  $RO_2$  isomers to  $QOOH$  isomers and reactions of peroxyalkylhydroperoxides ( $QOOH - O_2$ ) forming ketohyperoxides.
- During the second stage,  $\tau_{e,f}$  is characterized by reactions that relate to the hydrogen chemistry.

## References

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- [5] Diamantis D J, Kyritsis D C and Goussis D A, *2nd Intl. Conference in Model Reduction in Reacting Flows*, 2009