

Do we understand how two-stage hydrocarbon ignition mechanisms work?



6th International Conference on Chemical Kinetics

July 25-29, 2005

National Institute of Standards and Technology
Gaithersburg, MD

Andrei Kazakov, Zhenwei Zhao, Bradley D. Urban, and Frederick L. Dryer
Department of Mechanical and Aerospace Engineering, Princeton University,
Princeton NJ 08544; email: andrei@Princeton.EDU



Ongoing Debate and Controversy

Westbrook (2000)

... it is tempting to try to simplify these kinetic systems to make them easy to understand. A linear model is frequently most satisfying. A leads to B leads to C. In these kinetic problems, several processes happen together to cause the thermal runaway of ignition, and it is not clear that any of them can be identified as the "cause." It is most useful to recall the different processes that occur and the conditions required for each of them."

Peters et al. (2002)

... This interpretation differs from that of Westbrook ...

... only 12 of the reactions in the 30-step short mechanism are rate determining, of which a subset of four different reactions controls the low temperature and the high temperature regime ...

Griffiths et al. (2005a, b)

... Peters et al. (2002) claimed that the most of the second stage of two-stage ignition occurred when OH radicals can no longer be removed by the primary fuel. This is not so for n-butane combustion ...

... Principal routes to heat release in the transition "plateau" region involve the molecular intermediates kinetically linked to formaldehyde and hydrogen peroxide rather than primary fuel ...

Motivation and Background

Kinetics of low-temperature oxidation of large hydrocarbons exhibits:

- Two-stage ignition
- Turnover Temperature and negative temperature coefficient behavior
- Cool flames

Implications:

- Practical: understanding (and control) of ignition in combustion driven energy conversion devices
- fundamental: interesting kinetic behavior - challenging problem!

Initial phenomenological interpretations:

- Frank-Kamenetskii (1940) - simple 4-step isothermal kinetic scheme exhibiting oscillations
- Sokolov (1948) - ideas of formaldehyde feedback
- Yang and Gray (1969) - simple kinetic scheme with thermal feedback
 - extremely successful in predicting main kinetic features
 - inclusion of an exothermic termination step was one of the key items
 - More followed (reviewed by Griffiths, 1995)

Benson (1981)

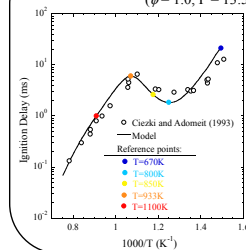
- Comprehensive mechanistic analysis in terms of specific elementary processes
- among main points
 - Competition between $R \cdot O_2 \leftrightarrow RO_2$ and $R \cdot O_2 \rightarrow olefin + HO_2$ provides the switch from branching to non-branching behavior with the temperature increase
 - For molecules C6 or larger, the isomerization sequence provides an intramolecular branching sequence ...

Detailed reaction mechanisms for large hydrocarbons

- Started to appear in mid-1980s build around Benson's ideas and have been under continuous development
- n-heptane is one of the most studied
 - although detailed reaction schemes are increasingly available and exercised routinely, their kinetic complexity (and size) hinder phenomenological interpretation and understanding!

Case Study

"standard" n-heptane/air ignition case
($\phi = 1.0, P = 13.5$ bar)



*experimental conditions and the shock-tube data of Czekci and Adomeit (1993) are used to validate virtually all low-temperature n-heptane mechanisms in existence

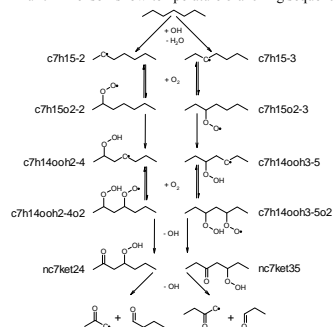
*NTC behavior is observed between the initial temperatures 800 and 930 K

Model

Detailed reaction mechanism n-heptane oxidation of Curran et al. (1998, 2004)

- 561 species participating in 2539 reactions
- used as a starting point or reaction database for most of detailed and reduced models in the literature
- readily available for download

Built-in Benson's low-temperature branching sequence:



Although comprehensive isomeric sets were included in the model, two pathways shown above are typically most important:

*abstractions from second and third carbon dominate over those from first and fourth due to bond strength and degeneracy issues, respectively

*2-4 and 3-5 isomerizations dominate over other possibilities due to transition state ring strain considerations used to estimate these rates

Methods

- conventional flux and sensitivity analysis
- eigenvalue analysis (Computational Singular Perturbation, Lam 1993):

Chemical kinetic ODE system: $\frac{d\mathbf{z}}{dt} = \mathbf{g}(\mathbf{z}, \mathbf{T})$, where $\mathbf{z} = (\bar{T}, y_1, y_2, \dots, y_n)^T$, \bar{T} - normalized temperature; y_i - species mass fractions (n total); \mathbf{g} - vector of rates defined by reaction mechanism

For a local Jacobian matrix, $\mathbf{J} = \frac{d\mathbf{g}}{d\mathbf{z}}$, one can define a transformation $\mathbf{J} = \mathbf{V}\mathbf{\Lambda}\mathbf{V}^{-1}$, where

$\mathbf{V} = (\mathbf{v}_1, \mathbf{v}_2, \dots, \mathbf{v}_n)$ - matrix of eigenvectors of \mathbf{J} , $\mathbf{\Lambda}$ - diagonal matrix containing eigenvalues of \mathbf{J}

The rate vector can be decomposed into sum of modal contributions:

$$\mathbf{g}(\mathbf{z} + \Delta\mathbf{t}) \approx \sum_{i=1}^n f_i \mathbf{v}_i \exp(\lambda_i \Delta\mathbf{t})$$

f_i - mode amplitude, indicates mode importance at current time t

λ_i - mode eigenvalue, indicates mode timescale and physical behavior:

$\text{Re}(\lambda_i) < 0$ - stable (decaying) mode; $\text{Re}(\lambda_i) > 0$ - unstable (explosive) mode - associated with ignition

$\text{Im}(\lambda_i) \neq 0$ - oscillatory mode

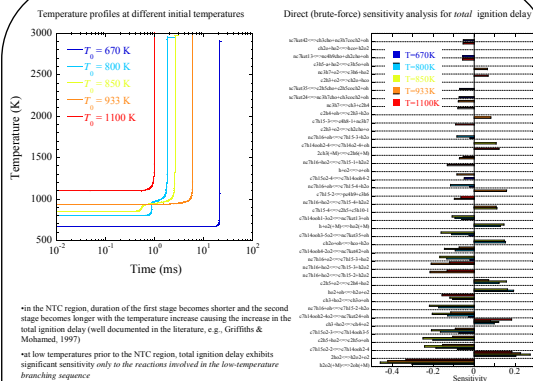
CSP is ideally suited for the analysis of ignition problem:

- more "direct" analysis of kinetic ODE system as opposed to the sensitivity
- identifying and following the explosive modes allows determination of the factors controlling ignition unambiguously
- in conjunction with flux analysis, complete interpretation can be derived

Practical implementation

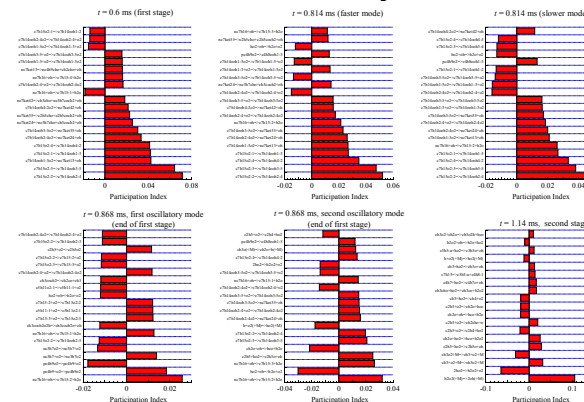
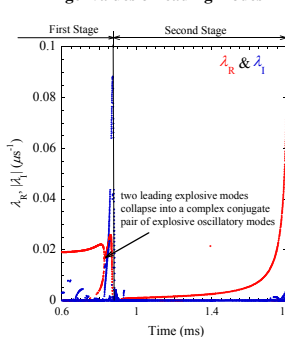
- in-house software package coupled with CHEMKIN library for post-processing of SENKIN outputs is developed
- unlike most prior implementations, temperature is included in the variable vector (important for thermal feedback)
- eigenvalue analysis is performed using LAPACK's facilities

Initial Observations



CSP Analysis Example: Case of $T_0 = 800$ K

Eigenvalues of leading modes



Interpretation based on CSP and Flux Analysis

First Stage

As expected, in the beginning of the first stage of ignition, the system evolution toward ignition is entirely driven by the low-temperature branching sequence. During this period, the system exhibits a single, dominant explosive mode. The major rate-controlling steps are the intramolecular isomerizations, c7H15o2-2 <-> c7H15ooh2-4 and c7H15o2-2 <-> c7H15ooh2-4.

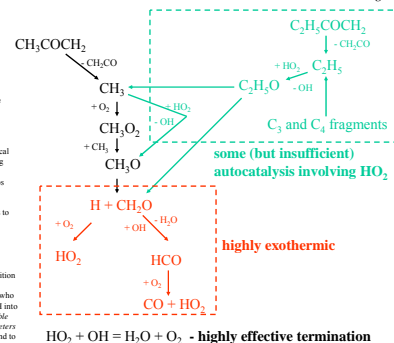
End of First Stage

The interpretation of the system behavior at the end of the first stage is very complicated. Prior to the end of the stage, in addition to the existing dominant explosive mode, another slower explosive mode with a lower amplitude appears. Immediately after its appearance, this new mode grows increasingly faster until its timescale reaches that of the first dominant mode. From that point, the two explosive modes collapse into a complex conjugate pair of explosive oscillatory modes. After a short period of acceleration, the real component of the pair's eigenvalues decreases passing through zero, and the modes lose their explosive nature, indicating the end of the first stage. The identification of the physical nature of the second mode is not straightforward; it appears to have nearly the same set of contributing reactions as seen in the first one. The complementary reaction heat flux analysis suggests that this second mode is associated with the emerging heat release coming from a sequence of exothermic steps involved in formation and oxidation of formaldehyde leading to generation of HO₂ (see Figure on the left). Although this sequence is extremely exothermic, it also produces large quantities of HO₂, which results in very effective chain termination via HO₂ + OH = H₂O + O₂. This chain termination appears to be one of the major factors responsible for the process slowdown at the end of the first stage.

Second Stage

During the second stage, the system is also characterized by a single, dominant explosive mode. The explosive mode is mainly (and nearly exclusively) controlled by degenerate branching via decomposition of H₂O₂, H₂O₂ = OH + OH. This result is generally consistent with a conventional point of view (Westbrook, 2000; Battin-Leclerc et al., 2005b) but contradicts the conclusion of Peters et al. (2002) who interpreted the runaway at the end of the second stage "as a consequence of the sudden release of OH into non-steady state, once the fuel is depleted". No reactions of fuel and OH were found to have noticeable contributions to the explosive mode. Therefore, based on the present CSP analysis, the argument of Peters et al. can be conclusively rejected. The other factors of importance during the second stage were found to be the termination reaction HO₂ + H₂O = H₂O₂ + O₂ and a number of secondary branching and termination reactions involving C₂ and C₃ species. It also appears that the second stage ignition has primarily chain-branching character, and the importance of thermal feedback implied by Westbrook (2000) is somewhat exaggerated.

Heat release and Chain Termination Mechanism at the End of First Stage



References

- Battin-Leclerc, F., Balleu, F., Fairweather, M., Glauco, P.A., Griffiths, J.F., Hughes, K.J., Peter, R., Tomlin, A.S. "A Numerical Study of the Kinetic Origin of Two-Stage Autoignition and the Dependence of Autoignition Temperature on Reaction Pressure in Low-Alkane Air Mixtures", European Combustion Meeting, Louvain-la-Neuve, Belgium, April 3-6, 2005.
- Benson, S.W. *Prog. Energy Combust. Sci.* 7, 125-134 (1981).
- Czekci, H. and Adomeit, G. *Combust. Flame* 93, 421-433 (1993).
- Curran, H.J., Gaffuri, P., Pitz, W.J., Westbrook, C.K. *Combust. Flame* 114, 149-177 (1998); also 2004 version of the mechanism at <http://www-cm.umd.gov/combustion/combustion2.html>.
- Frank-Kamenetskii, D. A. Zh. Fiz. Khim. 14, 30 (1940).
- Griffiths, J.F., Hughes, K.J., Peter, R. *Prog. Combust. Sci.* 30, 1083-1091 (2004a).
- Griffiths, J.F. *Prog. Energy Combust. Sci.* 21, 25-107 (1995).
- Griffiths, J.F., Molodetskii, C. in *Low-Temperature Combustion and Autoignition*, (Pilling, M.J., Ed.), Chapman & Elsevier, New York, 1997.
- Lam, S.H. *Combust. Sci. Technol.* 89, 375-404 (1993).
- Peters, N., Poulakis, G., Sauer, R., Schladt, K. *Combust. Flame* 128, 38-59 (2002).
- Safilakos, I. V. Dakti Akad. Nauk SSSR, 60, 405 (1948).
- Westbrook, C. K. *Proc. Combust. Inst.* 28, 1563-1577 (2000) and the discussion section therein.
- Yang, C.H., Gray, B.F. *J. Phys. Chem.* 73, 3395 (1969); Yang, C.H., Gray, B.F. *Trans. Faraday Soc.* 65, 1644 (1969).

Acknowledgment

This work has been supported by NASA Grant NCC3-375 and by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy under Grant No. DE-FG02-86ER13503.