A Detailed Low-Temperature Reaction Mechanism of n-Heptane Auto-Ignition

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ABSTRACT

A reaction mechanism for the description of C_1 to C_4 combustion has been combined with a mechanism for heptane oxidation derived from group additivity rules. It turns out that the main chain branching processes relevant for engine knock in the temperature range around 850 K are connected with the addition of a second O_2 molecule to species generated by the alkyl + $O_2 \leftrightarrow RO_2$ equilibrium and can predict negative temperature coefficients near 850 K. The results of simulations are compared with measurements as far as possible.

INTRODUCTION

The subject of this work is the understanding of auto-ignition. Two topics have been given special consideration:

(1) General work on the C_7H_{16} reaction mechanism (detailed analysis of the alkyl radical peroxide equilibrium and its temperature dependence, second oxidation of oxygen-containing species by O_2 reaction to lead to additional chain-branching at low temperatures less than 900 K, consistency of the reaction rate coefficients involved in these mechanisms)

(2) Determination of temperature dependence of ignition delay times with help of this detailed mechanism with special consideration of the low temperature part showing a negative or at least an unusual temperature dependence to understand corresponding experimental results.

As far as possible, results of the simulations have been compared with experimental data from shock tubes and adiabatic compression engines.

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CONSERVATION EQUATIONS AND SOLUTION

Calculation of ignition delay times (or induction times) is performed by solving the conservation equations of the reaction system, considering the respective experimental conditions of pressure, volume, and temperature which, in some cases (e. g. end-gas of Otto engines), are time-dependent. Treating homogeneous mixtures, these equations represent then a system of ordinary differential equations with the time t as independent variable and with the species concentrations c_i as dependent variables. The equation system may be written as (see [1,2])

$$\dot{c}_i = \omega_i + c_i \cdot \left\{ \frac{\dot{p}}{p} - \frac{RT \cdot \Sigma \dot{\omega}_i}{p} - \frac{\dot{T}}{T} \right\} \quad ; \quad i = 1,...,n$$

if the temperature T and the pressure p are given, or in the alternative formulation

$$\dot{c}_i = \omega_i - c_i \cdot \frac{\dot{V}}{V} \quad ; \quad i = 1,...,n$$

if the temperature T and the volume V are given, with ω_i = molar rate of formation of species i, R = gas constant, n_s = number of species (typically ~100 for large hydrocarbons); $c_i(t=t_0) = c_{i0}$ are the initial conditions.

For the given system of ordinary differential equations for the concentrations and their derivatives

$$\vec{c} = (c_1,...,c_{n_s})^T \quad ; \quad \vec{c}'(t) = f[t,\vec{c}(t),\vec{p}]^T$$

with the system parameters p_j, j=1,...,m (e. g. the rate coefficients), differentiation with respect to the parameter vector $\vec{p}$ yields then the linear equation system for the $(n_s \times m)$ matrix S of sensitivity coefficients $S_{ij}(t) = \partial c_i(t)/\partial p_j$

$$S'(t) = J(t) \cdot S(t) + f_p(t)$$

where J(t) is the Jacobian matrix and $f_p(t)$ are the $n_s \times m$ matrix of local parametric derivatives which easily can be evaluated by numerical differentiation:

$$f_{pij}(t) = \left(\frac{\partial f_i}{\partial p_j} \right)_{p_{k \neq j}, c}$$

with initial values which are given by the expressions at the start time of integration

$$S(t = t_0) = \frac{\partial c_0(p)}{\partial p} \quad ; \quad c_0 = c(t = 0)$$

Solution of this initial value problem is obtained by use of the programs DASSL [3] or LIMEX [4,5], both of them designed to solve stiff differential/algebraic systems. Solution of the additional sensitivity equations is performed simultaneously with the solution of the model equations [6,7].

HIGH TEMPERATURE REACTION MECHANISM

The reaction mechanism used in this paper is based on a critical review on ~400 elementary reactions which may occur in hydrocarbon combustion [8-10]. Unimportant reactions are eliminated by comparison of the rates of reaction in the flames considered here. Details are explained elsewhere [9].

The extensive literature on the hydrogen-oxygen- and the hydrogen-oxygen-carbon monoxide reaction system [8,11-13] shall not be discussed here in detail, since there are several comprehensive reviews on the elementary reaction and rate coefficients in this system [8-10].

In the same way, combustion of C_1- to C_8-hydrocarbons [9,14] can be described by detailed reaction schemes consisting of elementary steps. In lean and moderately rich combustion, the hydrocarbon is attacked by O, H, OH, and HO_2 in the first step. These radicals are produced by the chain-branching steps of the oxyhydrogen reaction. Chain branching at high temperature (T > 1100 K at P = 1 bar) is predominantly provided by

$$H\bullet \quad + \quad O_2 \quad \rightarrow \quad OH\bullet \quad + \quad O\bullet$$
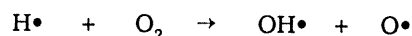
The alkyl radicals formed in this way decompose to smaller alkyl radicals by fast thermal elimination of alkenes. Only the relatively slow thermal decomposition of the smallest alkyl radicals (CH_3 and C_2H_5) competes with recombination and with oxidation reactions by O and O_2 which are very important processes in ignition. This part of the reaction mechanism is rate-controlling in the combustion of alkanes and alkenes, and is therefore the reason for the similarity of all alkane and alkene flames.
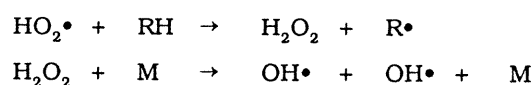
LOW TEMPERATURE REACTION MECHANISM

The full C_7H_{16} oxidation mechanism resulting cannot been listed here for lack of space (~20 pages computer outprint). Including the combination of $\bullet C_7H_{15}$ radicals

with a first O_2 molecule (but not yet with a second one as described below), an older version of the reaction mechanism has been delivered recently [15].

Ignition mainly is governed by chain branching processes which are rather unspecific of the fuel considered at high temperature, whereas they are fuel specific at low temperature, leading to very complex reaction systems if the numerous different isomeric structures are taken into consideration.
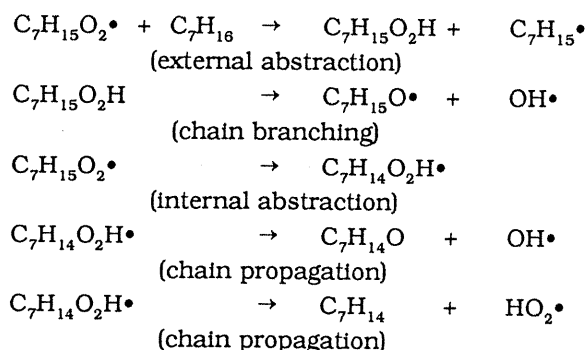
At medium temperature (1100 K > T > 900 K at a pressure p = 1 bar), additional chain branching behaviour is introduced by the following reaction sequence (here R• = alkyl radical):

$$HO_2\bullet \quad + \quad RH \quad \rightarrow \quad H_2O_2 \quad + \quad R\bullet$$
$$H_2O_2 \quad + \quad M \quad \rightarrow \quad OH\bullet \quad + \quad OH\bullet \quad + \quad M$$

At low temperature (T < 900 K at p = 1 bar), there is so-called "degenerated chain-branching", characterized by the fact that a main precursor of chain-branching (here: $RO_2\bullet$ radicals) is decomposed at higher temperature, leading to an inverse temperature dependence of reaction rate. In the case of n-heptane (R=C_7H_{15} isomers), the resulting reaction mechanism ("→" denotes irreversible reaction, "↔" reversible reaction; the points denote the radical species) is given by:

$$C_7H_{15}\bullet \quad + \quad O_2 \quad \leftrightarrow \quad C_7H_{15}O_2\bullet$$
(first O_2 addition)
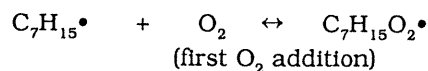
where the temperature dependence of the equilibrium constant leads to decomposition at temperatures above ~800 K, thus leading to degenerate branching. The $C_7H_{15}O_2\bullet$ formed can undergo external or internal H atom abstraction:

$$C_7H_{15}O_2\bullet \quad + \quad C_7H_{16} \quad \rightarrow \quad C_7H_{15}O_2H \quad + \quad C_7H_{15}\bullet$$
(external abstraction)

$$C_7H_{15}O_2H \quad \rightarrow \quad C_7H_{15}O\bullet \quad + \quad OH\bullet$$
(chain branching)

$$C_7H_{15}O_2\bullet \quad \rightarrow \quad C_7H_{14}O_2H\bullet$$
(internal abstraction)

$$C_7H_{14}O_2H\bullet \quad \rightarrow \quad C_7H_{14}O \quad + \quad OH\bullet$$
(chain propagation)

$$C_7H_{14}O_2H\bullet \quad \rightarrow \quad C_7H_{14} \quad + \quad HO_2\bullet$$
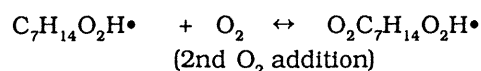(chain propagation)

This means that external H atom abstraction leads to pronounced chain branching, whereas internal H atom abstraction (via ring formation) only leads to chain propagation.
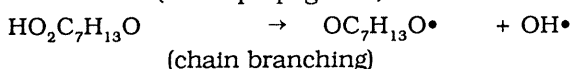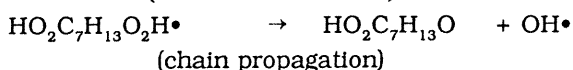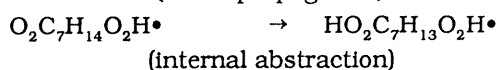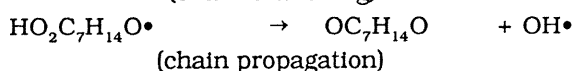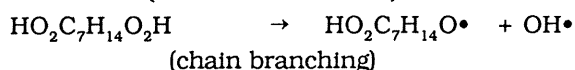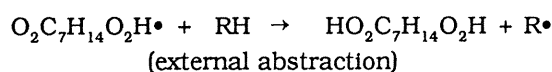
All simulations at conditions of interest here show the internal H atom abstraction to be the reaction path preferred, if the rate coefficients taken from the literatu-

re are used (see [15] for further reference). Thus, no distinct acceleration of the ignition process can be expected as result of the first O_2 attack, as it is known from experiments of different groups (see below).

As a consequence, the second attack of O_2 is considered in detail, as it is used for example in the simplified formal mechanisms describing low temperature ignition (see e. g. [16,17]):

$$C_7H_{14}O_2H\bullet \quad + \quad O_2 \quad \leftrightarrow \quad O_2C_7H_{14}O_2H\bullet$$
$$(2nd \ O_2 \ addition)$$

Again, the $O_2C_7H_{14}O_2H\bullet$ radical formed can undergo external or internal H atom abstraction:

$$O_2C_7H_{14}O_2H\bullet + RH \rightarrow HO_2C_7H_{14}O_2H + R\bullet$$
$$(external \ abstraction)$$
$$HO_2C_7H_{14}O_2H \rightarrow HO_2C_7H_{14}O\bullet + OH\bullet$$
$$(chain \ branching)$$
$$HO_2C_7H_{14}O\bullet \rightarrow OC_7H_{14}O + OH\bullet$$
$$(chain \ propagation)$$
$$O_2C_7H_{14}O_2H\bullet \rightarrow HO_2C_7H_{13}O_2H\bullet$$
$$(internal \ abstraction)$$
$$HO_2C_7H_{13}O_2H\bullet \rightarrow HO_2C_7H_{13}O + OH\bullet$$
$$(chain \ propagation)$$
$$HO_2C_7H_{13}O \rightarrow OC_7H_{13}O\bullet + OH\bullet$$
$$(chain \ branching)$$

In contrary to the first O_2 attack, this means that both external H atom abstraction and internal H atom abstraction lead to chain propagation. Thus, a distinct acceleration of the ignition process should be expected as result of the second O_2 attack, explaining the experiments (see below).

SIMULATION RESULTS

The simulated dependence of ignition delay time from temperature around the transition region is shown in Fig. 1.

Typical is the transition between high temperature and low temperature, taking place between 750 K and 950 K. Sensitivity analysis shows that this transition is due to the fact that the degenerate chain branching mechanism is determined by the second combination reaction of O_2 with $C_7H_{14}O_2H\bullet$ in its different isomeric forms.

The equilibrium $C_7H_{14}O_2H\bullet + O_2 \leftrightarrow O_2C_7H_{14}O_2H\bullet$ lies on the $O_2C_7H_{14}O_2H\bullet$ side at low temperature, leading to the chain branching steps

$$HO_2C_7H_{14}O_2H \rightarrow HO_2C_7H_{14}O\bullet + OH\bullet$$
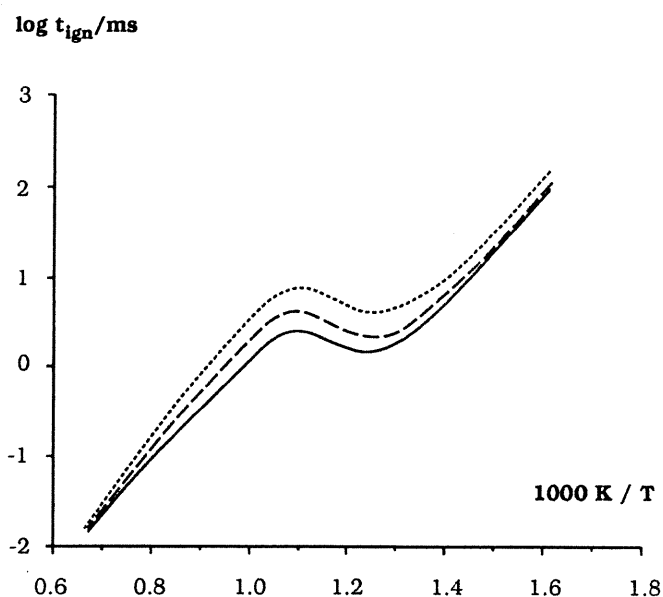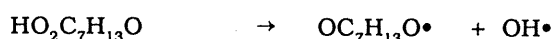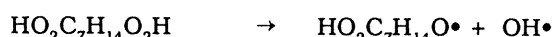$$HO_2C_7H_{13}O \rightarrow OC_7H_{13}O\bullet + OH\bullet$$

Fig.1: Calculated ignition delay times as function of the mixture temperature (p = 13.6 bar) for different equivalence ratios Φ = 2.0 (——), Φ = 1.0 (---), and Φ = 0.5 (·····)

and on the $C_7H_{14}O_2H\bullet + O_2$ side at high temperature, thus preventing chain branching.
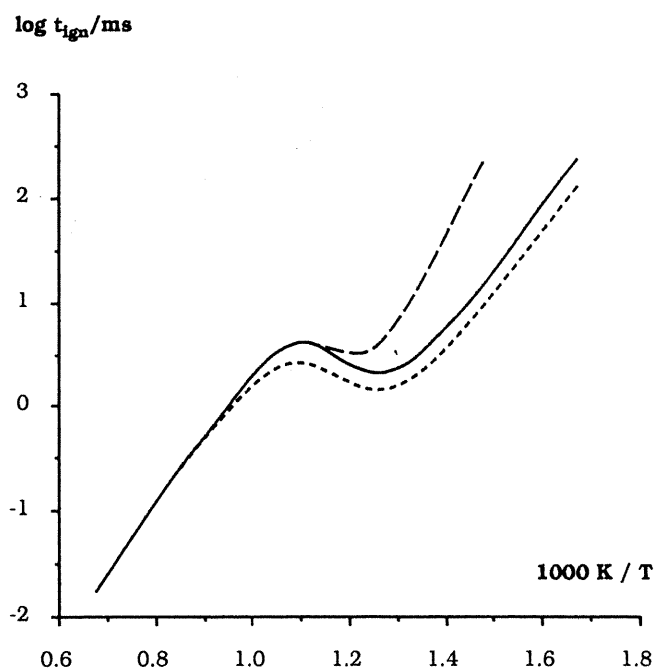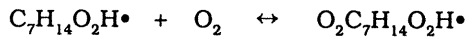

Fig.2: Influence of rate coefficient variations on the negative temperature coefficient region; —— final mechanism, ····· faster 2nd O_2 addition, ----- slower internal H atom abstraction

The position of the transition region mainly is dependent on the equilibrium constants of the 2nd O_2 addition

$$C_7H_{14}O_2H\bullet \ + \ O_2 \ \leftrightarrow \ O_2C_7H_{14}O_2H\bullet$$

and on the subsequent internal H atom abstraction reaction

$$O_2C_7H_{14}O_2H\bullet \ \leftrightarrow \ HO_2C_7H_{13}O_2H\bullet$$
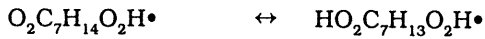
Acceleration of the 2nd O_2 addition will shorten the induction time in the low temperature range and will slightly shift it to higher temperatures. On the other hand, lowering the internal H atom abstraction rate coefficient will strongly increase the induction times in the low temperature region and reduce the width of the negative temperature coefficient range (see Fig. 2).

This is confirmed by the results of a sensitivity analysis given in Fig. 3. The outstanding rate limiting reactions are the formation of the dihydroxyalkyl radical (internal isomerization) and its decomposition.
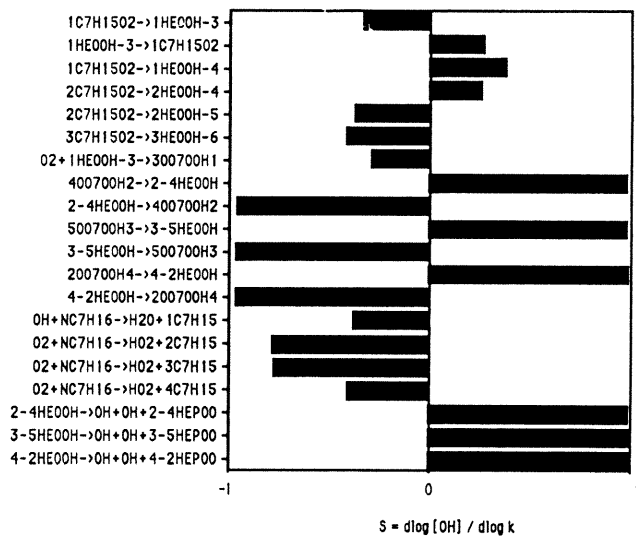

Fig.3: Sensitivity analysis with respect to OH radical formation during the induction period at p = 20 bar, T = 650 K

COMPARISON WITH EXPERIMENTS

A comparison with shock tube experiments [18] is given in Fig. 4, showing reasonable agreement. Similar experimental results with negative temperature exponent are known for heptane-octane mixtures [19].

In all cases, there is (both in experiments and simulations) the typical negative temperature exponent transition region, which can be explained quantitatively with the reaction mechanism described above.
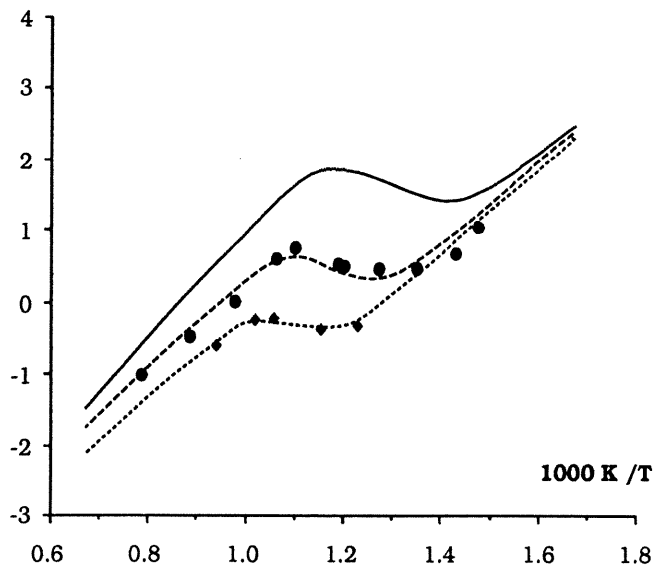

Fig.4: Comparison of some selected experimental (points; see [18]) and simulated (lines) ignition delay times t_{ign} as function of temperature at p = 3 bar (——), 13.6 bar (---), and 40 bar (·····), stoichiometric mixture $\Phi = 1$

ACKNOWLEDGEMENT

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