Hydrogen-Oxygen Induction Times Above Cross-Over Temperatures

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Abstract: Ignition in hydrogen-oxygen systems above cross-over temperatures and under varius conditions of pressure and composition is addressed computationally and by asymptotic methods. Through numerical calculations for isobaric, homogeneous and adiabatic hydrogen-air mixtures it is shown that the detailed chemistry can be reduced to only six elementary steps for determining induction times over the range of conditions addressed. Then, an analytical expression for ignition time dependent on temperature, pressure and composition is derived which agree well with computational results. It is shown that O and OH maintain steady state during ignition for stoichiometric and fuelrich mixtures, while H maintain a steady state for sufficiently fuel-lean conditions. Simple asymptotic formulas for the induction times are derived for these two limits that demonstrate the limiting effect of O_2 under rich conditions and H_2 under lean conditions

Key words: Hydrogen-oxygen ignition times, cross-over temperatures, short-mechanism, analytical induction time, asymptotic analysis.

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Above the second explosion limit, the ignition of hydrogen-air mixtures is known to exhibit a relatively long period of chain-carrier growth prior to significant heat release, which occurs through chain recombination once a sufficiently large radical pool has formed. Since this induction period typically represents a considerable fraction of the overall combustion time, designs of hydrogen combustion devices must account for this delay.

Numerous shock-tube experimental measurements of hydrogen-air induction times are available in the literature. The criteria used in experiments for defining the induction time vary. Under most conditions, in contrast to ignition of many others fuels, the resulting value of the induction time in hydrogen-oxygen systems depends relatively weakly on the definition used.

In this work four different mechanisms are used for calculation of ignition histories by numerical integration of the conservation equations for species and energy in a homogeneous mixture at constant pressure. Results of such detailed-chemistry computations are compared with experimental measurements. Figure 1 shows comparisons with shock-tube experimental induction times measured by Just and Schmalz and Bhaskaran et al.

Because of the low radical concentrations, six elementary steps suffice to describe accurately the induction period:

$$\begin{array}{c} H_2 + O_2 \stackrel{0}{\longrightarrow} HO_2 + H \\ H_2 + O_2 \stackrel{1}{\longrightarrow} OH + OH \\ H + O_2 \stackrel{2}{\longrightarrow} O + OH \\ H_2 + O \stackrel{3}{\longrightarrow} OH + H \\ H_2 + OH \stackrel{4}{\longrightarrow} H_2O + H \\ H + O_2 + M \stackrel{5}{\longrightarrow} HO_2 + M \end{array}$$

The temperature increment and the reactant consumption occurring during the induction period are small and can be therefore neglected when writing the dimensionless evolution equations for the radicals corresponding to the 6-step short mechanism defined above:

$$\frac{dy_{H}}{d\tau} = -(\varepsilon + 1/2)y_{H} + y_{O} + y_{OH} + v_{0}$$
(1)

$$\frac{dy_o}{d\tau} = \frac{\phi}{\kappa_o} (y_H / 2 - y_o)$$
⁽²⁾

$$\frac{dy_{OH}}{d\tau} = \frac{\phi}{\kappa_{OH}} (y_H / 2 + y_O - y_{OH} + v_1)$$
(3)

In the formulation, $\phi = c_{H_2}/2c_{o_2}$ represents the equivalence ratio of the mixture, with c_{O_2} and c_{H_2} denoting the initial concentrations of hydrogen and oxygen. The radical concentrations have been scaled according to $y_H = 2c_H/c_{H_2}$, $y_o = c_o/(\kappa_o c_{O_2})$ and

 $y_{OH} = c_{OH}/(\kappa_{OH}c_{O_2})$. Use is made of the characteristic branching time of reaction 2 to define the dimensionless time $\tau = 2k_2c_{O_2}t$. Correspondingly, the reaction rates enter in the formulation through the ratios $v_0 = k_1/k_2$, $v_1 = 2k_0/k_2$, $\varepsilon = k_5c_M/2k_2$, $\kappa_0 = k_2/k_3$, $k_{OH} = k_2/k_4$. Herein, ignition is identified as the instant when $y_0y_{OH}/y_H = K_2\phi/(\kappa_0\kappa_{OH})$, with the radical concentration obtained from (1)-(3).

The exact solution of the linear equations (1)-(3) for $\tau >> 1$ simplifies to $A_1Y_1 \exp(\lambda_1\tau)$, in terms the positive real eigenvalue λ_1 and its associated eigenvector $Y_1 = (1, Y_O, Y_{OH})$ giving the following expression for the induction time:

$$t_i = \frac{1}{2k_2 c_{O_2} \lambda_1} Ln \left(\frac{K_2 \phi}{\kappa_O \kappa_{OH}} \frac{1}{Y_{OH} Y_O A_1} \right)$$
(4)

Simplified expressions for t_i can be sought in the limit of rich and lean mixtures by using asymptotic methods. For rich mixtures, $\phi \gg 1$, the leading order of such an asymptotic analysis turn out to be equivalent to introducing steady-state assumptions for the radicals *O* and *OH*, obtaining the following expression for the induction time:

$$t_{R} = \frac{1}{2k_{2}c_{O_{2}}(1-\varepsilon)}Ln\left(\frac{2K_{2}\phi}{\kappa_{O}\kappa_{OH}}\frac{1-\varepsilon}{\nu_{0}+\nu_{1}}\right)$$
(5)

For lean mixtures, $\phi \ll 1$, the leading order solution of the asymptotic development is in this case equivalent to introducing a steady state assumption for H. Solving the problem for $\bar{\tau} \gg 1$, in terms of the alternative dimensionless time $\bar{\tau} = \tau \phi = k_2 c_{H_2} t$, gives

$$t_{L} = \frac{1}{k_{2}c_{H_{2}}\lambda_{1}} Ln \left(\frac{2K_{2}\phi}{\kappa_{O}\kappa_{OH}} \frac{4}{\nu_{0}} \frac{1 + \sqrt{\kappa_{OH}/(2\kappa_{O})}}{1 + \nu_{1}/\nu_{0} + \sqrt{2\kappa_{OH}/\kappa_{O}}} \right)$$
(6)

for the induction time of lean mixtures, where

$$\lambda_{1} = \frac{\left[2(1+\varepsilon)\kappa_{O}\kappa_{OH} + \varepsilon^{2}(\kappa_{O} + \kappa_{OH})^{2}\right]^{1/2} - \varepsilon(\kappa_{O} + \kappa_{OH})}{\kappa_{O}\kappa_{OH}\left(1+2\varepsilon\right)}$$
(7)

Induction times at atmospheric pressure obtained from the exact solution (4) of equations (1)-(3) are compared in Figure 2 with asymptotic predictions for rich (5) and lean mixtures (6) and with those obtained with the detailed-chemistry description by integrating the full conservation equations for energy and species. Figure 2 indicates that in the intermediate range $0.07 \le \phi \le 1$ all three radicals are out of steady state. The corresponding induction time evolves from the fuel-limited value (6) corresponding to lean mixtures to the oxidizer-limited solution of rich mixtures given in (5).



Figure 1. Variation with temperature of the induction time as obtained from detailed-chemistry numerical calculations (solid lines: SD mechanism, dotted lines: Maas & Warnatz, dashed lines: GRI mechanism, dot-dashed lines: Miller and Bowman), while the symbols denote the shock-tube experimental results of Just and Schmalz (p=0.41, 0.43, 1.41 atm) and of Bhaskaran et al. (p=2.5 atm).



Figure 2. The induction time at atmospheric pressure as obtained from integration of the full conservation equations (solid lines), from evaluation of the exact solution to (1)-(3) given in equation (4) (dashed lines), and from evaluations of the asymptotic predictions given in (5) and (6) (dotted lines).