A Numerical Investigation on the Chemical Kinetics Process of a Reacting n-Dodecane Spray Flame under Compression Ignition Combustion Condition

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Supplemental Material

Captions

S1. Calculation for the reaction rate constants.

S1. Calculation for the reaction rate constants

The general elementary chemical reaction can be described as

\[
\sum_{k=1}^{K} v_{kl} S_{pk} \leftrightarrow \sum_{k=1}^{K} v'_{kl} S_{pk} \quad (i = 1, ..., I)
\]  

where \( v_{kl} \) represents the stoichiometric coefficient for the \( i^{th} \) reaction, \( S_{pk} \) represents chemical species symbol for the \( k^{th} \) species, \( v' \) and \( v'' \) are forward and reverse stoichiometric coefficients, respectively, and \( I \) represents the total reaction number.

For a non-three-body reaction, the production rate for each species is calculated by,

\[
\dot{\omega}_k = \sum_{i=1}^{I} v_{kl} q_i \quad (k = 1, ..., K)
\]  

\[
v_{kl} = v'_{kl} - v''_{kl}
\]  

\[
q_i = k_{fi} \prod_{k=1}^{K} [X_k]^{v_{ki}} - k_{ri} \prod_{k=1}^{K} [X_k]^{v''_{ki}}
\]  

where \( q_i \) represents rate of progress variable for the \( i^{th} \) reaction, \( X_k \) represents molar concentration for the \( k^{th} \) species, \( k_{fi} \) and \( k_{ri} \) are forward and reverse rate constants for the \( i^{th} \) reaction, and \( K \) represents the total species number.
The production rate for each species can also be calculated by,

\[ \dot{\omega}_k = \dot{C}_k - \dot{D}_k \]  

\[ \dot{C}_k = \sum_{i=1}^{l} v_{ki} k_i \prod_{j=1}^{K} [X_j]^{v_{ji}} + \sum_{i=1}^{l} v_{ki} f_i \prod_{j=1}^{K} [X_j]^{v_{ji}} \]  

\[ \dot{D}_k = \sum_{i=1}^{l} v_{ki} k_i \prod_{j=1}^{K} [X_j]^{v_{ji}} + \sum_{i=1}^{l} v_{ki} r_i \prod_{j=1}^{K} [X_j]^{v_{ji}} \]  

where \( \dot{C}_k \) and \( \dot{D}_k \) represent formation and destruction rates for the \( k^{th} \) species, respectively.

However, for a three-body reaction, the items (\( q_i, \dot{C}_k, \dot{D}_k \)) should be multiplied by a third-body concentration,

\[ [M] = \sum_{k=1}^{K} \alpha_{ki} [X_k] \]  

where \( \alpha_{ki} \) is a third-body factor.

For reversible reactions, the forward rate constant (\( k_{fi} \)) follows the Arrhenius temperature dependence,

\[ k_{fi} = A_i T^{\beta_i} \exp \left( \frac{-E_i}{R T} \right) \]  

where \( A_i \) is pre-exponential factor, \( T \) is temperature, \( \beta_i \) is temperature exponent, \( E_i \) is activation energy, and \( R \) is universal gas constant (unit in cal.).

The reverse rate constant (\( k_{ri} \)) is calculated through its relationship with \( k_{fi} \) and equilibrium constants by,

\[ k_{ri} = \frac{k_{fi}}{k_{ei}} \]  

\[ k_{ei} = k_{pi} \left( \frac{P_{atm}}{R T} \right)^{\sum_{k=1}^{K} v_{ki}} \]  

\[ k_{pi} = \exp \left( \frac{\Delta S_0^0}{R} - \frac{\Delta H_0^0}{R T} \right) \]  

\[ \frac{\Delta S_0^0}{R} = \sum_{k=1}^{K} S_{ki}^0 \]  

\[ \frac{\Delta H_0^0}{R T} = \sum_{k=1}^{K} h_{ki}^0 \]  

where \( k_{ei} \) and \( k_{pi} \) are equilibrium constants, \( P_{atm} \) is cell pressure (unit in atm), \( R \) is universal gas constant (unit in J), and \( \Delta S_0^0 \) and \( \Delta H_0^0 \) are entropy and enthalpy changes for the \( i^{th} \) reaction, respectively.

Specially, the reaction rate constants for the fall-off reactions (pressure-dependent) are described as a blending of rates at low- and high-pressure limits. For unimolecular/recombination fall-off
reactions, it is defined as,

\[ k = k_\infty \frac{P_r}{1 + P_r} F \]  

(15)

For chemically activated bimolecular reactions, it is defined as,

\[ k = k_0 \frac{1}{1 + P_r} F \]  

(16)

where in equations (15) and (16), \( k_\infty \) and \( k_0 \) represent high- and low-pressure limits, respectively, and \( P_r \) is reduced pressure, which is defined as,

\[ P_r = \frac{k_d[M]}{k_\infty} \]  

(17)

In addition, \( F \) is fall-off blending factor and defined to be unity in Lindemann form [1], and in Troe form it is defined as,

\[ F = (F_{cent})^{1 + \left( \frac{A_{Troe}}{B_{Troe}} \right)^2} \]  

(18)

\[ F_{cent} = (1 - \alpha)e^{-\left( \frac{T}{T^*} \right)} + \alpha e^{-\left( \frac{T}{T^*} \right)} + e^{-\left( \frac{T^*}{T} \right)} \]  

(19)

\[ A_{Troe} = \log_{10} P_r - 0.67 \log_{10} F_{cent} - 0.4 \]  

(20)

\[ B_{Troe} = 0.806 - 1.1762 \log_{10} F_{cent} - 0.14 \log_{10} P_r \]  

(21)

where \( \alpha, T^*, T^{**}, \) and \( T^{***} \) are specified Troe parameters. Specially, when \( T^{**} \) is omitted in the chemical mechanism, the last term of \( F_{cent} \) in equation (19) is defined to be zero.

Based on the calculated production rates for each species, the HRRs for every cell and reaction can be calculated by,

\[ HRR = -\sum_{k=1}^{K} H_k^0 \omega_k \]  

(22)

\[ HRR_i = -\sum_{k=1}^{K} H_k^0 v_k i_q \]  

(23)

\[ \frac{H_k^0}{R} = a_{1k} + \frac{a_{2k}}{2} T + \frac{a_{3k}}{3} T^2 + \frac{a_{4k}}{4} T^3 + \frac{a_{5k}}{5} T^4 + \frac{a_{6k}}{6} T^5 \]  

(24)

\[ \frac{S_k^0}{R} = a_{1k} \ln T + a_{2k} T + \frac{a_{3k}}{2} T^2 + \frac{a_{4k}}{3} T^3 + \frac{a_{5k}}{4} T^4 + a_{7k} \]  

(25)

where \( H_k^0 \) and \( S_k^0 \) are standard molar enthalpy and entropy for each species, respectively, which are calculated through the standard seven-coefficient polynomial method, and \( a_{1k} \) to \( a_{7k} \) are coefficients from the thermodynamic data.

S2. Table S1

**Table S1.** Reactions 281 to reactions 288.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>R281</td>
<td>H + O₂ → O + OH</td>
</tr>
<tr>
<td>R282</td>
<td>O + H₂ → H + OH</td>
</tr>
<tr>
<td>R283</td>
<td>O + H₂O → 2OH</td>
</tr>
<tr>
<td>R284</td>
<td>OH + H₂ → H + H₂O</td>
</tr>
<tr>
<td>R285</td>
<td>H + OH + M → H₂O + M</td>
</tr>
<tr>
<td>R286</td>
<td>H + O₂(+M) → HO₂(+M)</td>
</tr>
<tr>
<td>R287</td>
<td>HO₂ + O → OH + O₂</td>
</tr>
<tr>
<td>R288</td>
<td>HO₂ + H → 2OH</td>
</tr>
</tbody>
</table>

**References**