Supporting Information: Plasma-based CH₄ Conversion into Higher Hydrocarbons and H₂: Modeling to Reveal the Reaction Mechanisms of Different Plasma Sources

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1. Detailed model description

1.1 General description

The conservation equations (1) in a 0D model are solved for all species:

\[
\frac{dn_s}{d\tau} = \sum_{i=1}^{j} [ (a_{s,i}^R - a_{s,i}^L) R_i ]
\]

where \( n_s \) is the density of species \( s \) (in cm\(^{-3}\)), \( j \) the total number of reactions in which that particular species is produced or consumed, \( a_{s,i}^L \) and \( a_{s,i}^R \) the stoichiometric coefficients at the left hand side and right hand side of a particular reaction equation, and \( R_i \) the rate of that reaction (in cm\(^{-3}\) s\(^{-1}\)), given by:

\[
R_i = k_i \prod_s n_s^{a_{s,i}}
\]

where \( k_i \) is the rate constant (in cm\(^3\) s\(^{-1}\) or cm\(^6\) s\(^{-1}\) for two-body or three-body reactions, respectively) and \( a_{s,i} \) was defined above. The rate constants of the heavy particle reactions are either constant or dependent on the gas temperature, whereas the rate constants of the electron impact reactions depend on the electron temperature \( T_e \) or the reduced electric field \( \frac{E}{N} \) (i.e., the electric field \( E \) divided by the number density of all neutral species \( N \), usually expressed in Td = 10\(^{-17}\) V cm\(^2\)). The rate constants of the electron impact reactions are generally calculated according to the following equation:

\[
k_i = \int_{\epsilon_{th}}^{\infty} \sigma_i(\epsilon) \nu(\epsilon) f(\epsilon) d\epsilon
\]
with ε the electron energy (usually in eV), ε_{th} the minimum threshold energy needed to induce the reaction, v(ε) the velocity of the electrons (in cm s^{-1}), σ_i(ε) the cross section of collision i (in cm^2), and f(ε) the (normalized) electron energy distribution function (EEDF; in eV^{-1}) calculated using a Boltzmann solver. The reactions included in the model, along with their rate coefficients and the references where these data are adopted from, are listed in Tables S.2-S.5.

In this work we use the ZDPlaskin code^1 to solve the balance equations (1) of all species. This code also has a built-in Boltzmann solver, called BOLSIG+^2, to calculate the EEDF and the rate constants of the electron impact reactions based on a set of cross sections, the plasma composition, the gas temperature and the reduced electric field (E/N).

The electric field (E; in V cm^{-1}) is calculated from a given power density, using the so-called local field approximation^3:

\[ E = \frac{P}{\sqrt{\sigma}} \]  \hspace{1cm} (4)

with P the input power density (in W cm^{-3}) and σ the plasma conductivity (A V^{-1} cm^{-1}). The plasma conductivity is estimated at the beginning of the simulations as^3:

\[ \sigma = \frac{10^4 e^2 n_{e,\text{init}}}{m_e v_m} \]  \hspace{1cm} (5)

with e the elementary charge (1.6022x10^{-19} C), n_{e,\text{init}} the initial electron density (in cm^{-3}), m_e the electron mass (9.1094x10^{-31} kg) and ν_m the collision frequency (in s^{-1}) calculated using BOLSIG+. During the simulation the plasma conductivity is calculated as^3:

\[ \sigma = \frac{e v_d n_e}{(E/N)_{\text{prev}} n_0} \]  \hspace{1cm} (6)

with v_d the electron drift velocity (in cm s^{-1}), which is calculated using BOLSIG+ implemented in ZDPlaskin, and (E/N)_{\text{prev}} the reduced electric field at the previous time step (in V cm^2).
The balance equation for the gas temperature $T_{gas}$ (in K) is also solved, in case of the MW plasma:

$$N_{\gamma - 1} \frac{dT_{gas}}{dt} = P_{e,el} + \sum_j R_j \Delta H_j - P_{ext}$$  \hspace{1cm} (7)

where $N = \sum n_i$ is the total neutral species density, $\gamma$ is the specific heat ratio of the total gas mixture, $k$ is the Boltzmann constant, $P_{e,el}$ is the gas heating power density due to elastic electron-neutral collisions (in W cm$^{-3}$), $R_j$ is the rate of reaction $j$ (in cm$^{-3}$ s$^{-1}$), $\Delta H_j$ is the heat released (or consumed when this value is negative) by reaction $j$ (in J) and $P_{ext}$ is the heat loss due to energy exchange with the surroundings (in W cm$^{-3}$). The latter one is originally calculated as:

$$P_{ext} = \frac{8\lambda}{R^2}(T_{gas} - T_{gas,\gamma})$$  \hspace{1cm} (8)

where $\lambda$ is the gas thermal conductivity of CH$_4$ (in W cm$^{-1}$ K$^{-1}$), $R$ the radius of the plasma zone, which is near the reactor wall in a reduced pressure MW plasma, such as in the work of Heintze et al.\textsuperscript{4} and it is at 0.6 cm in the atmospheric MW plasma of Shen et al.\textsuperscript{5} as predicted by Berthelot et al.\textsuperscript{6} $T_{gas}$ is the plasma gas temperature and $T_{gas,i}$ the plasma gas temperature near the edge of the plasma zone, which is typically the average of room temperature and the plasma gas temperature, according to Berthelot.\textsuperscript{6} The gas thermal conductivity of CH$_4$ is taken from Afshar et al.\textsuperscript{7} which is a function of gas temperature, i.e.

$$\lambda(W \text{ cm}^{-1} \text{ K}^{-1}) = 10^{-5}( - 23.35 + 0.1698T_{gas} + 1.893 \times 10^{-5}T_{gas}^2)$$  \hspace{1cm} (9)

The specific heat ratio of the total (ideal) gas mixture is calculated from the specific heat ratios of the individual species in the model, $\gamma_i$, using the formula:

$$N_{\gamma - 1} \frac{\gamma}{\gamma - 1} = \sum_i n_i \frac{\gamma_i}{\gamma_i - 1}$$  \hspace{1cm} (10)
where \( n_i \) are the densities of the individual species \( i \). The specific heat ratio of CH\(_4\) is taken to be 1.32, 1.23 for C\(_2\)H\(_2\), 1.24 for C\(_2\)H\(_4\), 1.19 for C\(_2\)H\(_6\), 1.13 for C\(_3\)H\(_8\) and 1.15 for C\(_3\)H\(_6\) \(^8\). Diatomic species, i.e. H\(_2\) and CH, have a specific heat ratio equal to 1.4 and the other species not mentioned above, 1.67, just as in Kozak and Bogaerts. \(^9\).

For the DBD and the GAP, we did not solve the above equation for the gas temperature, because we had data available from experiments in the DBD \(^10\) and more detailed 2D/3D calculations for the GAP \(^11\).

1.2 Vibrational and Rotational Energy Transfer of CH\(_4\)

CH\(_4\) has four degenerate vibrational modes: the \( \nu_1 \) singly degenerate symmetric stretch mode (lowest level at 0.362 eV), the \( \nu_2 \) doubly degenerate scissoring bend mode (lowest level at 0.190 eV), the \( \nu_3 \) triply degenerate asymmetric stretch mode (lowest level at 0.374 eV) and the \( \nu_4 \) triply degenerate umbrella bend mode (lowest level at 0.162 eV) \(^12\). In our model we incorporate only these lowest levels as a first approximation. Also, two rotational levels (\( J_3 \) and \( J_4 \)) with energies equal to 0.0078 eV and 0.013 eV, respectively, are included \(^13,14\). The relaxation between these modes and rotational relaxation was studied by Menard-Bourcin et al. \(^15\) but only at 193 K and 296 K. Based on earlier works about vibrational and rotational relaxation of Capitelli et al. \(^16\), Wang and Springer \(^17\), and Richards and Sigafoos \(^18\), we assume, as a first approximation, that these rate constants follow the relation:

\[
\frac{k_{T_2}}{k_{T_1}} = \exp \left( -aT_2^{-\frac{1}{2}} + aT_1^{-\frac{1}{2}} \right)
\]

(11)

Where \( k_{T_1} \) and \( k_{T_2} \) are the rate coefficients (in cm\(^3\) s\(^{-1}\)) at gas temperatures \( T_1 \) and \( T_2 \) (in K) (\( T_2 > T_1 \)), respectively, and \( a \) is a constant, which is calculated, based on the rate coefficients at gas temperatures equal to 193 K and 296 K. The reverse reactions are also included based on detailed balance, which was suggested by Menard-Bourcin et al. \(^15\).
1.3 Vibrational kinetics of $\text{H}_2$

In the model, 14 vibrational levels are included till the dissociation limit (4.48 eV), together with ground state $\text{H}_2$. The energies of these levels are calculated using the expression of an anharmonic oscillator for a diatomic molecule with $\omega_e = 4401.213 \text{ cm}^{-1}$ and $\omega_e x_e = 121.336 \text{ cm}^{-1}$.

Table S.1: Vibrational levels of $\text{H}_2$ included in the model and corresponding energies.

<table>
<thead>
<tr>
<th>Level</th>
<th>$\Delta E_v$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000</td>
</tr>
<tr>
<td>1</td>
<td>0.516</td>
</tr>
<tr>
<td>2</td>
<td>1.001</td>
</tr>
<tr>
<td>3</td>
<td>1.457</td>
</tr>
<tr>
<td>4</td>
<td>1.882</td>
</tr>
<tr>
<td>5</td>
<td>2.277</td>
</tr>
<tr>
<td>6</td>
<td>2.642</td>
</tr>
<tr>
<td>7</td>
<td>2.977</td>
</tr>
<tr>
<td>8</td>
<td>3.282</td>
</tr>
<tr>
<td>9</td>
<td>3.557</td>
</tr>
<tr>
<td>10</td>
<td>3.802</td>
</tr>
<tr>
<td>11</td>
<td>4.017</td>
</tr>
<tr>
<td>12</td>
<td>4.201</td>
</tr>
<tr>
<td>13</td>
<td>4.356</td>
</tr>
<tr>
<td>14</td>
<td>4.480</td>
</tr>
</tbody>
</table>

1.3.1 VV-relaxation $\text{H}_2-\text{H}_2$

For $\text{H}_2-\text{H}_2$ VV-relaxation processes, i.e., $\text{H}_2(v + 1) + \text{H}_2(w) \rightarrow \text{H}_2(v) + \text{H}_2(w + 1)$, the approach of Matveyev and Silakov \cite{20} is used to scale the rate coefficient of the reaction involving the lowest levels $k_{1,0}^{0,1}$ (in cm$^3$ s$^{-1}$) to rate coefficients of reactions involving higher levels $k_{v+1,w+1}^{w,w+1}$:

\[
k_{v+1,w+1}^{w,w+1} = k_{1,0}^{0,1}(v + 1)(w + 1)\left[2^{\frac{3}{2}} - \frac{1}{2} \exp\left(-\delta|w - v|\right)\right]g(v,w) \quad (12)
\]

Where:

\[
\delta = 0.21\sqrt{T_{\text{gas}}/300} \quad (13)
\]

And:

\[
\]
The correction function $g(v,w)$ which applies for $w > v$ is computed from:

$$g(v,w) = \exp \left[ \Delta_1 (w - v) - \Delta_2 (w - v)^2 \right]$$

(15)

In which:

$$\Delta_1 = 0.236 \left( \frac{T_{\text{gas}}}{300} \right)^{\frac{1}{4}}$$

(16)

And:

$$\Delta_2 = 0.0572 \left( \frac{300}{T_{\text{gas}}} \right)^{\frac{1}{4}}$$

(17)

### 1.3.2 VT-relaxation $H_2$

For VT- relaxation mechanisms, i.e., $H_2(v) + M \rightarrow H_2(v \pm 1) + M$, we use the same scaling law as suggested in Matveyev and Silakov \(^{20}\) to calculate the rate coefficients $k_{v,v-1}$ for relaxation from higher levels from the rate coefficient for VT-relaxation of the first vibrational level towards ground state $k_{1,0}$:

$$k_{v,v-1} = k_{1,0} \exp \left( \delta_{VT}(v - 1) \right)$$

(18)

Where

$$\delta_{VT} = 0.97 \left( \frac{T_{\text{gas}}}{300} \right)^{\frac{1}{4}}$$

(19)

The expression for $k_{1,0}$ is taken from Capitelli et al. \(^{16}\):

$$k_{1,0} = 7.47 \times 10^{-12} T_{\text{gas}}^{0.5} \exp \left( -93.87 T_{\text{gas}}^{-\frac{3}{2}} \right) \left[ 1 - \exp \left( -\frac{E_{1,0}}{T_{\text{gas}}} \right) \right]^{-1}$$

(20)

With $E_{1,0} = 5983 \, K$. The reverse processes are also included by using detailed balance.
The process in which H is the collision partner, \( H_2(v) + H \rightarrow H_2(w) + H \), has a different rate coefficient. This process comprises two processes, one of non-reactive character and another of reactive character. In the former the species collide and bounce apart, while in the latter, an atomic exchange takes place between the species. The rate coefficients for both processes are given in Gorse et al. but only for \( w < v < 10 \) since for these cases the VT relaxation with other species will dominate. The total rate coefficient is:

\[
k = A_n r \exp \left( -\frac{E_{a,nr}}{T_{\text{gas}}} \right) + A_r \exp \left( -\frac{E_{a,r}}{T_{\text{gas}}} \right) \tag{21}
\]

Where the pre-exponential factors, i.e. \( A_n r \) and \( A_r \) (in cm\(^3\) s\(^{-1}\)), and activation energies \( E_{a,nr} \) and \( E_{a,r} \) (in K) are given in Gorse et al. for all relaxation mechanisms from all levels \( v \) to all levels \( w \).

### 1.4 Full chemistry of pure CH\(_4\)

**Table S.2:** Electron impact reactions and their corresponding rate coefficients, either calculated using cross sections data, \( f(\sigma) \), or using an analytical expression, given in cm\(^3\) s\(^{-1}\) and cm\(^6\) s\(^{-1}\), for two-body and three-body reactions, respectively, as well as the references where the data are adopted from. Both \( T_{\text{gas}} \) and \( T_e \) are given in K.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>( e^- + CH_4(g) \rightarrow e^- + CH_4(g) )</td>
<td>( f(\sigma) )</td>
<td>24</td>
</tr>
<tr>
<td>( e^- + CH_4(j_3 - j_4) \rightarrow e^- + CH_4(j_3 - j_4) )</td>
<td>( f(\sigma) )</td>
<td>24</td>
</tr>
<tr>
<td>( e^- + CH_4(v_1 - v_4) \rightarrow e^- + CH_4(v_1 - v_4) )</td>
<td>( f(\sigma) )</td>
<td>24</td>
</tr>
<tr>
<td>( e^- + CH_4(g + j + v) \rightarrow 2e^- + CH_4^+ )</td>
<td>( f(\sigma) )</td>
<td>24</td>
</tr>
<tr>
<td>( e^- + CH_4(g + j + v) \rightarrow 2e^- + CH_4^+ + H )</td>
<td>( f(\sigma) )</td>
<td>25</td>
</tr>
<tr>
<td>( e^- + CH_4(g + j + v) \rightarrow e^- + CH_2^+ + H_2 )</td>
<td>( f(\sigma) )</td>
<td>25</td>
</tr>
<tr>
<td>( e^- + CH_4(g + j + v) \rightarrow e^- + CH_3 + H )</td>
<td>( f(\sigma) )</td>
<td>26,27</td>
</tr>
<tr>
<td>( e^- + CH_4(g + j + v) \rightarrow e^- + CH_2 + H_2 )</td>
<td>( f(\sigma) )</td>
<td>26,27</td>
</tr>
<tr>
<td>( e^- + CH_4(g + j + v) \rightarrow e^- + CH + H_2 + H )</td>
<td>( f(\sigma) )</td>
<td>26,27</td>
</tr>
<tr>
<td>( e^- + CH_4(g + j + v) \rightarrow e^- + C + 2H_2 )</td>
<td>( f(\sigma) )</td>
<td>26,27</td>
</tr>
<tr>
<td>( e^- + CH_4(g + j + v) \rightarrow e^- + CH_4(v_1) )</td>
<td>( f(\sigma) )</td>
<td>13,28</td>
</tr>
<tr>
<td>( e^- + CH_4(g + j + v) \rightarrow e^- + CH_4(v_2) )</td>
<td>( f(\sigma) )</td>
<td>13,28</td>
</tr>
<tr>
<td>( e^- + CH_4(g + j + v) \rightarrow e^- + CH_4(v_3) )</td>
<td>( f(\sigma) )</td>
<td>13,28</td>
</tr>
<tr>
<td>Reaction</td>
<td>Energy (eV)</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH_4(g + j) \rightarrow e^- + CH_4(v_i)$</td>
<td>$f(a)$ 13,28</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH_4 \rightarrow e^- + CH_4(j_3)$</td>
<td>$f(a)$ 13,28</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH_4 \rightarrow e^- + CH_4(j_4)$</td>
<td>$f(a)$ 13,28</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH_3 \rightarrow e^- + CH_3$</td>
<td>$f(a)$ 29</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH_3 \rightarrow 2e^- + CH_3^+$</td>
<td>$f(a)$ 25</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH_3 \rightarrow 2e^- + CH_2^+ + H$</td>
<td>$f(a)$ 25</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH_3 \rightarrow 2e^- + CH^+ + H_2$</td>
<td>$f(a)$ 25</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH_3 \rightarrow e^- + CH_2 + H$</td>
<td>$f(a)$ 26,27</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH_3 \rightarrow e^- + CH + H_2$</td>
<td>$f(a)$ 26,27</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH_3 \rightarrow e^- + C + H_2 + H$</td>
<td>$f(a)$ 26</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH_2 \rightarrow e^- + CH_2$</td>
<td>$f(a)$ 29</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH_2 \rightarrow 2e^- + CH_2^+$</td>
<td>$f(a)$ 25</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH_2 \rightarrow e^- + C + H$</td>
<td>$f(a)$ 26,27</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH_2 \rightarrow e^- + C + 2H$</td>
<td>$f(a)$ 26</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH \rightarrow e^- + CH$</td>
<td>$f(a)$ 29</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH \rightarrow 2e^- + CH^+$</td>
<td>$f(a)$ 25</td>
<td></td>
</tr>
<tr>
<td>$e^- + CH \rightarrow e^- + C + H$</td>
<td>$f(a)$ 26,27</td>
<td></td>
</tr>
<tr>
<td>$e^- + C \rightarrow e^- + C$</td>
<td>$f(a)$ 30,31</td>
<td></td>
</tr>
<tr>
<td>$e^- + C \rightarrow 2e^- + C^+$</td>
<td>$f(a)$ 26,27</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2 \rightarrow e^- + 2C$</td>
<td>$f(a)$ 26</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2 \rightarrow 2e^- + C_2^+$</td>
<td>$f(a)$ 26</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2 \rightarrow 2C$</td>
<td>$f(a)$ 1.93 x 10^{-6} T_e^{-0.5} 32</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_4 \rightarrow e^- + C_2H_6$</td>
<td>$f(a)$ 29</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_6 \rightarrow 2e^- + C_2H_5$</td>
<td>$f(a)$ 25</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_6 \rightarrow 2e^- + C_2H_5 + H$</td>
<td>$f(a)$ 25</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_6 \rightarrow 2e^- + C_2H_3^+ + H_2$</td>
<td>$f(a)$ 25</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_6 \rightarrow C_2H_5 + H$</td>
<td>$f(a)$ 33,34</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_6 \rightarrow C_2H_5 + C_2H_4 + H_2$</td>
<td>$f(a)$ 33,34</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_6 \rightarrow C_2H_5 + C_2H_4 + H_2$</td>
<td>$f(a)$ 34</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_6 \rightarrow e^- + C_2H_2 + 2H_2$</td>
<td>$f(a)$ 34</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_6 \rightarrow e^- + 2CH_3$</td>
<td>$f(a)$ 34</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_5 \rightarrow 2e^- + C_2H_5$</td>
<td>$f(a)$ 25</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_5 \rightarrow 2e^- + C_2H_4 + H$</td>
<td>$f(a)$ 25</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_5 \rightarrow 2e^- + C_2H_3 + H_2$</td>
<td>$f(a)$ 33,34</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_5 \rightarrow e^- + C_2H_4 + H$</td>
<td>$f(a)$ 33,34</td>
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</tr>
<tr>
<td>$e^- + C_2H_5 \rightarrow e^- + C_2H_3 + 2H$</td>
<td>$f(a)$ 34</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_5 \rightarrow e^- + C_2H_2 + H_2 + H$</td>
<td>$f(a)$ 34</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_5 \rightarrow e^- + C_2H_2 + H_2$</td>
<td>$f(a)$ 34</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_5 \rightarrow e^- + C_2H + 2H$</td>
<td>$f(a)$ 34</td>
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<tr>
<td>$e^- + C_2H_5 \rightarrow e^- + C_2H_2 + H$</td>
<td>$f(a)$ 34</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_5 \rightarrow e^- + C_2H + 2H$</td>
<td>$f(a)$ 34</td>
<td></td>
</tr>
<tr>
<td>$e^- + C_2H_5 \rightarrow e^- + C_2H_2 + H$</td>
<td>$f(a)$ 34</td>
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<td>$f(a)$ 29</td>
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<td>Rate Coefficient</td>
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<td>( 33,34 )</td>
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<tr>
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S10
\[
\begin{array}{|c|c|}
\hline
\text{reaction} & \text{rate coefficient} \ f(\sigma) \\
\hline
\text{2.57}\times10^{-7} & 33,34 \\
\hline
\end{array}
\]

\[
\begin{array}{|c|c|}
\hline
\text{reaction} & \text{rate coefficient} \ f(\sigma) \\
\hline
\text{2.57}\times10^{-7} & 33,34 \\
\hline
\end{array}
\]
\[ e^- + C_2H_6^+ \rightarrow C_2H_4 + 2H \] 3.36 \times 10^{-9} \left( \frac{300}{T_{\text{gas}}} \right)^{0.71} 34

\[ e^- + C_2H_5^+ \rightarrow C_2H_4 + H \] 7.70 \times 10^{-9} \left( \frac{300}{T_{\text{gas}}} \right)^{0.71} 34

\[ e^- + C_2H_5^+ \rightarrow C_2H_3 + 2H \] 1.92 \times 10^{-8} \left( \frac{300}{T_{\text{gas}}} \right)^{0.71} 34

\[ e^- + C_2H_5^+ \rightarrow C_2H_2 + H_2 + H \] 1.60 \times 10^{-8} \left( \frac{300}{T_{\text{gas}}} \right)^{0.71} 34

\[ e^- + C_2H_5^+ \rightarrow C_2H_2 + 3H \] 8.98 \times 10^{-9} \left( \frac{300}{T_{\text{gas}}} \right)^{0.71} 34

\[ e^- + C_2H_5^+ \rightarrow CH_3 + CH_2 \] 9.62 \times 10^{-9} \left( \frac{300}{T_{\text{gas}}} \right)^{0.71} 34

\[ e^- + C_2H_4^+ \rightarrow C_2H_3 + H \] 8.29 \times 10^{-9} \left( \frac{300}{T_{\text{gas}}} \right)^{0.71} 34

\[ e^- + C_2H_4^+ \rightarrow C_2H_2 + 2H \] 3.43 \times 10^{-8} \left( \frac{300}{T_{\text{gas}}} \right)^{0.71} 34

\[ e^- + C_2H_4^+ \rightarrow C_2H + H_2 + H \] 5.53 \times 10^{-9} \left( \frac{300}{T_{\text{gas}}} \right)^{0.71} 34

\[ e^- + C_2H_3^+ \rightarrow C_2H_2 + H \] 1.34 \times 10^{-8} \left( \frac{300}{T_{\text{gas}}} \right)^{0.71} 34

\[ e^- + C_2H_3^+ \rightarrow C_2H + 2H \] 2.74 \times 10^{-8} \left( \frac{300}{T_{\text{gas}}} \right)^{0.71} 34

\[ e^- + C_2H_2^+ \rightarrow C_2H + H \] 1.87 \times 10^{-8} \left( \frac{300}{T_{\text{gas}}} \right)^{0.71} 34

\[ e^- + C_2H_2^+ \rightarrow 2CH \] 4.87 \times 10^{-9} \left( \frac{300}{T_{\text{gas}}} \right)^{0.71} 34

\[ e^- + H_3^+ \rightarrow 3H \] \( f(\sigma) \) 39,40

\[ e^- + H_3^+ \rightarrow e^- + 2H + H^+ \] \( f(\sigma) \) 39

\[ e^- + H_3^+ \rightarrow e^- + H + H^+ \] \( f(\sigma) \) 40

\[ 2e^- + H_2^+ \rightarrow e^- + 2H \] \( \frac{3.17 \times 10^{21}}{6.022 \times 10^{23} T_e^{4.5}} \) 41

\[ 2e^- + H_3^+ \rightarrow e^- + H + H_2 \] \( \frac{3.17 \times 10^{21}}{6.022 \times 10^{23} T_e^{4.5}} \) 41

| Table S.3: | Ion-ion and ion-neutral reactions, as well as the references where the data are adopted from. The rate coefficients are given in cm\(^3\) s\(^{-1}\) and cm\(^6\) s\(^{-1}\), for two-body and three-body reactions, respectively. \(T_{\text{gas}}\) is given in K. |

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<th>Reaction</th>
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<th>Ref</th>
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<td>Comment</td>
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<td>Rate Constant (10^{-9} s^{-1})</td>
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<td>$H_2^+ + CH_2 \rightarrow CH_3^+ + H$</td>
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<td>$H_2^+ + C_2H_6 \rightarrow C_2H_2^+ + 3H_2$</td>
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<td>$H^+ + C_2H_2 \rightarrow C_2H_2^+ + H_2$</td>
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<td>$H^+ + C_2H \rightarrow C_2H^+ + H$</td>
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<tr>
<td>$H^+ + C_2H \rightarrow C_2H^+ + H_2$</td>
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</tbody>
</table>
\[
\begin{align*}
H^+ + C_2 &\rightarrow C_2^+ + H \\
H^+ + H_2 + M &\rightarrow H_3^+ + M \\
C_2^+ + C &\rightarrow C_2 + C^+
\end{align*}
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Ref</th>
</tr>
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<td>(CH_4(v_2) + M \leftrightarrow CH_4 + M)</td>
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<td>15</td>
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<td>(CH_4(v_4) + M \leftrightarrow CH_4 + M)</td>
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<td>(CH_4(v_3) + M \leftrightarrow CH_4(v_4) + M)</td>
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<td>(CH_4(v_4) + M \leftrightarrow CH_4 + M)</td>
<td>See section 1.2</td>
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<tr>
<td>(H_2(v + 1) + H_2(w) \rightarrow H_2(v) + H_2(w + 1))</td>
<td>See section 1.3.1</td>
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<tr>
<td>(H_2(v) + M \leftrightarrow H_2(v - 1) + M)</td>
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<td>(H_2(v) + H \leftrightarrow H_2(w) + H)</td>
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<td>(CH_4 + CH_2 \rightarrow 2CH_3)</td>
<td>(4.08 \times 10^{-18} T_{gas}^2 \exp(-\frac{4163}{T_{gas}}))</td>
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<td>(CH_4 + CH \rightarrow C_2H_4 + H)</td>
<td>(9.97 \times 10^{-11})</td>
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<td>(CH_4 + C_2H_5 \rightarrow C_2H_6 + CH_3)</td>
<td>(2.51 \times 10^{-15} \frac{T_{gas}^4}{R T_{gas}})</td>
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<td>(CH_4 + C_2H_3 \rightarrow C_2H_4 + CH_3)</td>
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<tr>
<td>(CH_4 + C_3H_7 \rightarrow C_3H_8 + CH_3)</td>
<td>(3.54 \times 10^{-16} \frac{T_{gas}^4}{R T_{gas}})</td>
<td>56</td>
</tr>
<tr>
<td>(CH_4 + C_3H_5 \rightarrow C_3H_6 + CH_3)</td>
<td>(1.71 \times 10^{-14} \frac{T_{gas}^4}{R T_{gas}})</td>
<td>57</td>
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<td>(CH_4 + H \rightarrow CH_3 + H_2)</td>
<td>(9.86 \times 10^{-13} \frac{T_{gas}^3}{R T_{gas}})</td>
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<td>(CH_4 + CH_3 \rightarrow H + C_2H_6)</td>
<td>(1.33 \times 10^{-10} \exp(-\frac{167.00}{R T_{gas}}))</td>
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<td>(CH_4 + C_4H_9 \rightarrow C_4H_{10} + CH_3)</td>
<td>(5.68 \times 10^{-17} \frac{T_{gas}^3}{R T_{gas}})</td>
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<td>(CH_4 + CH_2 \rightarrow C_2H_6)</td>
<td>(1.90 \times 10^{-12})</td>
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<tr>
<td>(CH_4 \rightarrow CH_3 + H)</td>
<td>(k_{\alpha}; 2.40 \times 10^{16} \exp(-\frac{52800}{T_{gas}}))</td>
<td>61</td>
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</tbody>
</table>

**Table S.4:** Neutral-neutral reactions, as well as the references where the data are adopted from. The rate coefficients are given in cm³ s⁻¹ and cm⁶ s⁻¹, for two-body and three-body reactions, respectively. \(T_{\text{gas}}\) is given in K. \(R\) is the gas constant (8.314 x 10⁻³ kJ mol⁻¹ K⁻¹). The \(\alpha\) parameter determines the effect of lowering the activation energy for reactions involving vibrationally excited levels of the molecules (see details in 46). The reactions with * are adjusted for a three-body collision by dividing by the total gas density. Reactions with both a low pressure rate constant \(k_0\) and high pressure rate constant \(k_{\alpha}\) are scaled using the Troe falloff formula (see details in 47, 48).
<table>
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<tr>
<th>Reaction</th>
<th>Rate Expression</th>
<th>Temperature (K)</th>
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<tr>
<td>$2\text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{H}$</td>
<td>$k_0 \cdot 1.40 \times 10^{-6} \exp \left( - \frac{45700}{T_{\text{gas}}} \right)$</td>
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<td>$2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$</td>
<td>$k_0 \cdot 1.20 \times 10^{-7} T_{\text{gas}}^{-1.18} \exp \left( - \frac{329.14}{T_{\text{gas}}} \right)$</td>
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<tr>
<td></td>
<td>$k_0 \cdot 1.87 \times 10^{-6} T_{\text{gas}}^{-7.03} \exp \left( - \frac{1390.54}{T_{\text{gas}}} \right)$</td>
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<tr>
<td>$\text{CH}_3 + \text{CH}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}$</td>
<td>$F_c \cdot 0.31 \exp \left( - \frac{T_{\text{gas}}}{90.0} \right)$ + $0.69 \exp \left( - \frac{T_{\text{gas}}}{2210} \right)$</td>
<td>7.1 x 10^{-11}</td>
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<tr>
<td>$\text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_4$</td>
<td>$F_c \cdot (1 - 0.619) \exp \left( - \frac{T_{\text{gas}}}{73.2} \right)$ + $0.619 \exp \left( - \frac{T_{\text{gas}}}{1180} \right)$ + $\exp \left( - \frac{9999}{T_{\text{gas}}} \right)$</td>
<td>5.00 x 10^{-11}</td>
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<tr>
<td>$\text{CH}_3 + \text{C}_2\text{H}_5 \rightarrow \text{C}_3\text{H}_8$</td>
<td>$k_0 \cdot 1.56 \times 10^{-11}$</td>
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<tr>
<td></td>
<td>$k_0 \cdot 1.49 \times 10^{-27} T_{\text{gas}}^{-16.82} \exp \left( - \frac{6575.24}{T_{\text{gas}}} \right)$</td>
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<tr>
<td>$\text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3 + \text{CH}_4$</td>
<td>$F_c \cdot (1 - 0.1527) \exp \left( - \frac{T_{\text{gas}}}{298} \right) + 0.15727 \exp \left( - \frac{T_{\text{gas}}}{2742} \right) + \exp \left( - \frac{7748}{T_{\text{gas}}} \right)$</td>
<td>2.18 x 10^{-11}</td>
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<tr>
<td>$\text{CH}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_4$</td>
<td>$2.18 \times 10^{-15} \frac{T_{\text{gas}}^4}{298} \exp \left( - \frac{34.67}{RT_{\text{gas}}} \right)$</td>
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<td>$\text{CH}_3 + \text{C}_2\text{H}_3 + \text{M} \rightarrow \text{C}_3\text{H}_6 + \text{M}$</td>
<td>$3.0 \times 10^{-13} \exp \left( - \frac{72.34}{RT_{\text{gas}}} \right)$</td>
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<td>$\text{CH}_3 + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_1 + \text{CH}_4$</td>
<td>$1.5 \times 10^{-11} \exp \left( - \frac{3.20}{RT_{\text{gas}}} \right)$</td>
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<td>$\text{CH}_3 + \text{C}_3\text{H}_6 \rightarrow \text{C}_3\text{H}_7 + \text{CH}_4$</td>
<td>$1.50 \times 10^{-24} \frac{T_{\text{gas}}^{3.65}}{298} \exp \left( - \frac{3600.40}{T_{\text{gas}}} \right)$</td>
<td>3.80 x 10^{-29}</td>
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<td>$\text{CH}_3 + \text{C}_3\text{H}_7 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_4$</td>
<td>$3.07 \times 10^{-12} \frac{T_{\text{gas}}^{0.32}}{298}$</td>
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<td>$1.68 \times 10^{-15} \frac{T_{\text{gas}}^{3.50}}{298} \exp \left( - \frac{23.78}{RT_{\text{gas}}} \right)$</td>
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<td>$\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$</td>
<td>$2.52 \times 10^{-14} \frac{T_{\text{gas}}^{3.12}}{298} \exp \left( - \frac{36.42}{RT_{\text{gas}}} \right)$</td>
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<td>$\text{CH}_3 + \text{H} \rightarrow \text{CH}_2 + \text{H}_2$</td>
<td>$1.00 \times 10^{-10} \exp \left( - \frac{63.19}{RT_{\text{gas}}} \right)$</td>
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<td>$\text{CH}_3 + \text{H} \rightarrow \text{CH}_4$</td>
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<tr>
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<tr>
<td>$CH_3 + C_3H_7 \rightarrow 2C_2H_5$</td>
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<td>$CH_3 + M \rightarrow CH_2 + H + M$</td>
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<td>$CH_3 + M \rightarrow CH + H_2 + M$</td>
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<tr>
<td>$CH_2 + C_3H_7 \rightarrow C_3H_6 + CH_3$</td>
<td>$3.01 \times 10^{-11}$</td>
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<tr>
<td>$CH_2 + C_3H_6 \rightarrow C_3H_5 + CH_3$</td>
<td>$1.20 \times 10^{-12} \exp \left( -\frac{25.94}{RT_{gas}} \right)$</td>
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<tr>
<td>$CH_2 + H_2 \rightarrow CH_3 + H$</td>
<td>$8.30 \times 10^{-19} T_{gas}^{2.00} \exp \left( -\frac{3938.65}{T_{gas}} \right)$</td>
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<tr>
<td>$CH_2 + H \rightarrow CH + H_2$</td>
<td>$1.00 \times 10^{-11} \exp \left( \frac{7.48}{RT_{gas}} \right)$</td>
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<tr>
<td>$CH_2 + M \rightarrow C + H_2 + M$</td>
<td>$2.16 \times 10^{-10} \exp \left( -\frac{247}{RT_{gas}} \right)$</td>
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<tr>
<td>$CH_2 + M \rightarrow CH + H + M$</td>
<td>$6.64 \times 10^{-9} \exp \left( -\frac{348}{RT_{gas}} \right)$</td>
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<tr>
<td>$2CH_2 \rightarrow C_2H_2 + H_2$</td>
<td>$2.66 \times 10^{-9} \exp \left( -\frac{6011.07}{T_{gas}} \right)$</td>
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<tr>
<td>$CH_2 + H \rightarrow CH_3$</td>
<td>$9.96 \times 10^{-10}$</td>
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<tr>
<td>$k_0: 5.74 \times 10^{-22} T_{gas}^{-2.76} \exp \left( -\frac{805.23}{T_{gas}} \right)$</td>
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<tr>
<td>$F_c: (1 - 0.562) \exp \left( -\frac{T_{gas}}{91} \right) + 0.562 \exp \left( -\frac{T_{gas}}{5836} \right) + \exp \left( -\frac{8552}{T_{gas}} \right)$</td>
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<tr>
<td>$CH + C_2H_6 \rightarrow C_3H_6 + H$</td>
<td>$3.00 \times 10^{-11}$</td>
<td></td>
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<tr>
<td>$CH + C_2H_6 + M \rightarrow C_3H_7 + M$</td>
<td>$1.14 \times 10^{-29}$</td>
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<tr>
<td>$CH + H_2 \rightarrow CH_2 + H$</td>
<td>$1.79 \times 10^{-10} \exp \left( -\frac{1565.17}{T_{gas}} \right)$</td>
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<tr>
<td>$CH + H \rightarrow C + H_2$</td>
<td>$4.98 \times 10^{-11}$</td>
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<tr>
<td>$CH + C_3H_3 \rightarrow C_2H_3 + H$</td>
<td>$4.98 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td>$CH + CH_2 \rightarrow C_2H_2 + H$</td>
<td>$6.64 \times 10^{-11}$</td>
<td></td>
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<tr>
<td>$CH + H_2 \rightarrow CH_3$</td>
<td>$3.29 \times 10^{-12} T_{gas}^{0.43} \exp \left( \frac{186.21}{T_{gas}} \right)$</td>
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<tr>
<td>$k_0: 1.33 \times 10^{-22} T_{gas}^{-2.80} \exp \left( -\frac{296.93}{T_{gas}} \right)$</td>
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<tr>
<td>Reaction</td>
<td>Rate Constant</td>
<td>References</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>---------------</td>
<td>------------</td>
</tr>
<tr>
<td>$CH + M \rightarrow C + H + M$</td>
<td>$3.16 \times 10^{-10}$</td>
<td>68</td>
</tr>
<tr>
<td>$CH + C_2H_3 \rightarrow CH_2 + C_2H_2$</td>
<td>$8.30 \times 10^{-11}$</td>
<td>73</td>
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<tr>
<td>$C + H_2 \rightarrow CH + H$</td>
<td>$6.64 \times 10^{-10}$</td>
<td>75</td>
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<tr>
<td>$C + CH_3 \rightarrow H + C_2H_2$</td>
<td>$8.30 \times 10^{-11}$</td>
<td>47.47</td>
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<tr>
<td>$C + CH_2 \rightarrow 2CH$</td>
<td>$2.69 \times 10^{-12}$</td>
<td>76</td>
</tr>
<tr>
<td>$C + CH_2 \rightarrow H + C_2H$</td>
<td>$8.30 \times 10^{-11}$</td>
<td>47, 47.47</td>
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<tr>
<td>$C + H_2 + M \rightarrow CH_2 + M$</td>
<td>$6.89 \times 10^{-32}$</td>
<td>77</td>
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<tr>
<td>$C_2H_6 + C_2H_3 \rightarrow C_2H_5 + C_2H_4$</td>
<td>$1.46 \times 10^{-13}$</td>
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<tr>
<td>$C_2H_6 + C_2H \rightarrow C_2H_2 + C_2H_5$</td>
<td>$5.99 \times 10^{-12}$</td>
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<tr>
<td>$C_2H_6 + C_3H_7 \rightarrow C_3H_6 + C_2H_5$</td>
<td>$1.19 \times 10^{-15}$</td>
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<tr>
<td>$C_2H_6 + C_3H_5 \rightarrow C_3H_6 + C_2H_5$</td>
<td>$5.71 \times 10^{-14}$</td>
<td>57</td>
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<tr>
<td>$C_2H_6 + H \rightarrow C_2H_2 + H_2$</td>
<td>$1.23 \times 10^{-11}$</td>
<td>54</td>
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<tr>
<td>$C_2H_6 + H \rightarrow CH_4 + CH_3$</td>
<td>$8.97 \times 10^{-20}$</td>
<td>78</td>
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<tr>
<td>$C_2H_6 \rightarrow 2CH_3$</td>
<td>$k_c: 1.80 \times 10^{21}$</td>
<td>61</td>
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<tr>
<td></td>
<td>$t_{gas}^{-1.24}$</td>
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<tr>
<td></td>
<td>$\exp \left(- \frac{45700}{T_{gas}} \right)$</td>
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<tr>
<td>$k_0: 4.50 \times 10^{-2}$</td>
<td>$\exp \left(- \frac{348}{T_{gas}} \right)$</td>
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<tr>
<td>$F_c: 0.54 \exp \left(- \frac{T_{gas}}{1250} \right)$</td>
<td>$\exp \left(- \frac{31.01}{T_{gas}} \right)$</td>
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<tr>
<td>$C_2H_6 + C_4H_5 \rightarrow C_4H_10 + C_2H_5$</td>
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<tr>
<td>$C_2H_6 + CH \rightarrow C_2H_4 + CH_3$</td>
<td>$1.79 \times 10^{-10}$</td>
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<tr>
<td>$C_2H_5 + CH_2 \rightarrow C_2H_5 + CH_3$</td>
<td>$9.00 \times 10^{-33}$</td>
<td>66</td>
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<tr>
<td>$2C_2H_5 \rightarrow C_2H_6 + C_2H_4$</td>
<td>$2.41 \times 10^{-12}$</td>
<td>54</td>
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<tr>
<td>$C_2H_5 + C_2H_4 \rightarrow C_2H_6 + C_2H_3$</td>
<td>$5.83 \times 10^{-14}$</td>
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<tr>
<td>$C_2H_5 + C_2H_2 \rightarrow C_2H_6 + C_2H$</td>
<td>$4.50 \times 10^{-13}$</td>
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<tr>
<td>$C_2H_5 + CH \rightarrow C_2H_4 + C_2H_2$</td>
<td>$3.01 \times 10^{-12}$</td>
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<tr>
<td>$C_2H_5 + C_3H_8 \rightarrow C_2H_6 + C_3H_7$</td>
<td>$1.61 \times 10^{-15}$</td>
<td>56</td>
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<tr>
<td>$C_2H_5 + C_3H_7 \rightarrow C_3H_8 + C_2H_4$</td>
<td>$1.91 \times 10^{-12}$</td>
<td>56</td>
</tr>
<tr>
<td>$C_2H_5 + C_3H_7 \rightarrow C_3H_6 + C_2H_6$</td>
<td>$2.41 \times 10^{-12}$</td>
<td>56</td>
</tr>
</tbody>
</table>
$$C_2H_5 + C_3H_6 \rightarrow C_3H_5 + C_2H_6$$

$$1.69 \times 10^{-15} \left( \frac{T_{\text{gas}}}{298} \right)^{3.50} \exp \left(- \frac{35.34}{RT_{\text{gas}}} \right)$$

$$C_2H_5 + H_2 \rightarrow C_2H_6 + H$$

$$4.12 \times 10^{-15} \left( \frac{T_{\text{gas}}}{298} \right)^{3.60} \exp \left(- \frac{27.77}{RT_{\text{gas}}} \right)$$

$$C_2H_5 + H \rightarrow 2\text{CH}_3$$

$$5.99 \times 10^{-11}$$

$$C_2H_5 + H \rightarrow C_2H_4 + H_2$$

$$3.32 \times 10^{-12}$$

$$C_2H_5 + H \rightarrow C_2H_6$$

$$k_\infty: 8.65 \times 10^{-7} T_{\text{gas}}^{-0.99} \exp \left(- \frac{795.17}{T_{\text{gas}}} \right)$$

$$k_0: 1.11 \times 10^{-6} T_{\text{gas}}^{-0.08} \exp \left(- \frac{3364.37}{T_{\text{gas}}} \right)$$

$$F_c(1 - 0.842) \exp \left( - \frac{T_{\text{gas}}}{125} \right) + 0.842 \exp \left( - \frac{T_{\text{gas}}}{2219} \right) + \exp \left(- \frac{6882}{T_{\text{gas}}} \right)$$

$$C_2H_5 \rightarrow C_2H_4 + H$$

$$k_\infty: 4.08 \times 10^{-12} T_{\text{gas}}^{-1.04} \exp \left(- \frac{154}{RT_{\text{gas}}} \right)$$

$$k_0: 2.99 \times 10^{-3} T_{\text{gas}}^{0.99} \exp \left(- \frac{167.12}{RT_{\text{gas}}} \right)$$

$$F_c(0.25 \exp \left(- \frac{T_{\text{gas}}}{97} \right) + 0.75 \exp \left(- \frac{T_{\text{gas}}}{1379} \right)$$

$$2C_2H_5 \rightarrow C_4H_{10}$$

$$9.55 \times 10^{-12}$$

$$C_2H_5 + C_4H_6 \rightarrow C_2H_4 + C_4H_{10}$$

$$1.40 \times 10^{-12}$$

$$C_2H_5 + C_2H_3 \rightarrow 2C_2H_4$$

$$4.42 \times 10^{-11}$$

$$C_2H_4 + C_2H \rightarrow C_2H_2 + C_2H_3$$

$$1.40 \times 10^{-10}$$

$$C_2H_4 + H \rightarrow C_2H_3 + H_2$$

$$9.00 \times 10^{-10} \exp \left(- \frac{62.36}{RT_{\text{gas}}} \right)$$

$$C_2H_4 + H \rightarrow C_2H_5$$

$$k_\infty: 9.68 \times 10^{-12} T_{\text{gas}}^{1.28} \exp \left(- \frac{5.40}{RT_{\text{gas}}} \right)$$

$$k_0: 3.31 \times 10^{-6} T_{\text{gas}}^{-0.62} \exp \left(- \frac{3507.80}{T_{\text{gas}}} \right)$$

$$F_c(1 - 0.975) \exp \left(- \frac{T_{\text{gas}}}{210} \right) + 0.975 \exp \left(- \frac{T_{\text{gas}}}{984} \right) + \exp \left(- \frac{4374}{T_{\text{gas}}} \right)$$

$$C_2H_4 + H_2 \rightarrow C_2H_5 + H$$

$$9.55 \times 10^{-12}$$

$$C_2H_4 + M \rightarrow C_2H_3 + H + M$$

$$4.30 \times 10^{-7} \exp \left(- \frac{404}{RT_{\text{gas}}} \right)$$

$$C_2H_4 + C_3H_6 \rightarrow C_3H_5 + C_2H_5$$

$$9.60 \times 10^{-11} \exp \left(- \frac{216}{RT_{\text{gas}}} \right)$$

$$C_2H_4 + C_2H_2 \rightarrow 2C_2H_3$$

$$4.00 \times 10^{-11} \exp \left(- \frac{286}{RT_{\text{gas}}} \right)$$

$$C_2H_4 + C_3H_6 \rightarrow C_3H_3 + C_3H_7$$

$$1.00 \times 10^{-10} \exp \left(- \frac{316}{RT_{\text{gas}}} \right)$$

$$2C_2H_4 \rightarrow C_2H_5 + C_2H_3$$

$$8.00 \times 10^{-10} \exp \left(- \frac{299}{RT_{\text{gas}}} \right)$$

$$C_2H_4 + CH_3 \rightarrow C_3H_7$$

$$k_\infty: 4.23 \times 10^{-18} T_{\text{gas}}^{1.60} \exp \left(- \frac{2868.65}{T_{\text{gas}}} \right)$$

$$k_0: 1.65 \times 10^{16} T_{\text{gas}}^{-14.60} \exp \left(- \frac{9144.44}{T_{\text{gas}}} \right)$$
<table>
<thead>
<tr>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_2H_4 \rightarrow C_2H_2 + H_2 )</td>
</tr>
<tr>
<td>( k_\infty: 8.00 \times 10^{12} T_{gas}^{0.44} \exp \left( -\frac{44675.39}{T_{gas}} \right) )</td>
</tr>
<tr>
<td>( k_0: 8.71 \times 10^{3} T_{gas}^{-0.30} \exp \left( -\frac{49219.93}{T_{gas}} \right) )</td>
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<tr>
<td>( F_c: (1 - 0.735) \exp \left( -\frac{T_{gas}}{180} \right) + 0.735 \exp \left( -\frac{T_{gas}}{1035} \right) + \exp \left( -\frac{5417}{T_{gas}} \right) )</td>
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<tr>
<td>( C_2H_4 + C_2H_5 \rightarrow C_4H_9 )</td>
</tr>
<tr>
<td>( 3.00 \times 10^{-14} \frac{T_{gas}^{2.48}}{298} \exp \left( -\frac{25.65}{R T_{gas}} \right) )</td>
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<tr>
<td>( C_2H_4 + H_2 \rightarrow C_2H_6 )</td>
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<tr>
<td>( 4.75 \times 10^{-16} \exp \left( -\frac{180}{R T_{gas}} \right) )</td>
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<tr>
<td>( C_2H_4 + CH_2 \rightarrow C_3H_6 )</td>
</tr>
<tr>
<td>( 5.30 \times 10^{-12} \exp \left( -\frac{2660}{R T_{gas}} \right) )</td>
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<tr>
<td>( C_2H_4 + C_4H_9 \rightarrow C_3H_6 + C_3H_7 )</td>
</tr>
<tr>
<td>( 5.00 \times 10^{-14} \exp \left( -\frac{25.53}{R T_{gas}} \right) )</td>
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<tr>
<td>( 2C_2H_3 \rightarrow C_2H_4 + C_2H_2 )</td>
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<tr>
<td>( 3.50 \times 10^{-10} )</td>
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<tr>
<td>( C_2H_3 + C_2H \rightarrow 2C_2H_2 )</td>
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<tr>
<td>( 3.15 \times 10^{-11} )</td>
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<td>( C_2H_3 + C_3H_8 \rightarrow C_4H_4 + C_3H_7 )</td>
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<tr>
<td>( 1.46 \times 10^{-13} \frac{T_{gas}^{3.30}}{298} \exp \left( -\frac{43.90}{R T_{gas}} \right) )</td>
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<td>( C_2H_3 + C_3H_7 \rightarrow C_2H_8 + C_2H_2 )</td>
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<tr>
<td>( 2.01 \times 10^{-12} )</td>
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<td>( C_2H_3 + C_3H_7 \rightarrow C_3H_6 + C_2H_4 )</td>
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<tr>
<td>( 2.01 \times 10^{-12} )</td>
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<tr>
<td>( C_2H_3 + C_3H_6 \rightarrow C_3H_5 + C_2H_4 )</td>
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<tr>
<td>( 1.68 \times 10^{-15} \frac{T_{gas}^{3.50}}{298} \exp \left( -\frac{19.62}{R T_{gas}} \right) )</td>
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<td>( C_2H_3 + C_4H_5 \rightarrow C_3H_6 + C_2H_2 )</td>
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<tr>
<td>( 8.00 \times 10^{-12} )</td>
</tr>
<tr>
<td>( C_2H_3 + H_2 \rightarrow C_2H_4 + H )</td>
</tr>
<tr>
<td>( 1.61 \times 10^{-13} \frac{T_{gas}^{2.03}}{298} \exp \left( -\frac{35.75}{R T_{gas}} \right) )</td>
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<tr>
<td>( C_2H_3 + H \rightarrow C_2H_2 + H_2 )</td>
</tr>
<tr>
<td>( 1.60 \times 10^{-10} )</td>
</tr>
<tr>
<td>( C_2H_3 + H \rightarrow C_2H_4 )</td>
</tr>
<tr>
<td>( k_\infty: 1.01 \times 10^{-11} T_{gas}^{0.27} \exp \left( -\frac{140.92}{T_{gas}} \right) )</td>
</tr>
<tr>
<td>( k_0: 7.72 \times 10^{-18} T_{gas}^{-3.86} \exp \left( -\frac{1670.86}{T_{gas}} \right) )</td>
</tr>
<tr>
<td>( F_c: (1 - 0.782) \exp \left( -\frac{T_{gas}}{207.5} \right) + 0.782 \exp \left( -\frac{T_{gas}}{2663} \right) + \exp \left( -\frac{6095}{T_{gas}} \right) )</td>
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<tr>
<td>( C_2H_3 \rightarrow C_2H_2 + H )</td>
</tr>
<tr>
<td>( k_\infty: 2.00 \times 10^{14} \exp \left( -\frac{20000}{T_{gas}} \right) )</td>
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<tr>
<td>( k_0: 6.90 \times 10^{17} T_{gas}^{-7.50} \exp \left( -\frac{22900}{T_{gas}} \right) )</td>
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<tr>
<td>( F_c: 0.35 )</td>
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<tr>
<td>( C_2H_3 + C_4H_9 \rightarrow C_2H_2 + C_4H_{10} )</td>
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<tr>
<td>( 1.40 \times 10^{-12} )</td>
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<tr>
<td>( C_2H_2 + H \rightarrow C_2H + H_2 )</td>
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<tr>
<td>( 1.00 \times 10^{-10} \exp \left( -\frac{93.12}{R T_{gas}} \right) )</td>
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<tr>
<td>( C_2H_2 + H \rightarrow C_2H_3 )</td>
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<tr>
<td>( k_\infty: 9.30 \times 10^{-12} \exp \left( -\frac{1207.85}{T_{gas}} \right) )</td>
</tr>
<tr>
<td>( k_0: 2.10 \times 10^{-7} T_{gas}^{-7.27} \exp \left( -\frac{3633.62}{T_{gas}} \right) )</td>
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<tr>
<td>Reaction</td>
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<tr>
<td>( C_2H_2 + H_2 \rightarrow C_2H_4 )</td>
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<tr>
<td>( C_2H_2 + H_2 \rightarrow C_2H_3 + H )</td>
</tr>
<tr>
<td>( C_2H_2 + M \rightarrow C_2H + H + M )</td>
</tr>
<tr>
<td>( 2C_2H_2 \rightarrow C_2H + C_2H_3 )</td>
</tr>
<tr>
<td>( C_2H_2 + CH_3 \rightarrow C_3H_5 )</td>
</tr>
<tr>
<td>( C_2H_2 + CH \rightarrow C_2H + CH_2 )</td>
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<tr>
<td>( C_2H_2 + C_4H_9 \rightarrow C_3H_6 + C_3H_5 )</td>
</tr>
<tr>
<td>( 2C_2H \rightarrow C_2H_2 + C_2 )</td>
</tr>
<tr>
<td>( C_2H + C_3H_9 \rightarrow C_2H_2 + C_3H_7 )</td>
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<tr>
<td>( C_2H + C_3H_7 \rightarrow C_2H_2 + C_3H_6 )</td>
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<tr>
<td>( C_2H + C_3H_6 \rightarrow C_2H_2 + C_3H_5 )</td>
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<tr>
<td>( C_2H + H_2 \rightarrow C_2H_2 + H )</td>
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<tr>
<td>( C_2H + H \rightarrow H_2 + C_2 )</td>
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<tr>
<td>( C_2H \rightarrow C_2H_2 )</td>
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<tr>
<td>Reaction</td>
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<tr>
<td>$C_3H_7 + C_3H_6 \rightarrow C_3H_5 + C_3H_8$</td>
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<tr>
<td>$C_3H_7 + C_3H_5 \rightarrow 2C_3H_6$</td>
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<tr>
<td>$C_3H_7 + H_2 \rightarrow C_3H_8 + H$</td>
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<tr>
<td>$C_3H_7 + H \rightarrow C_3H_6 + H_2$</td>
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<td>$C_3H_7 + H \rightarrow C_3H_8$</td>
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<td>$C_3H_7 + H \rightarrow CH_3 + C_2H_5$</td>
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<td>$C_3H_7 + M \rightarrow C_3H_6 + H + M$</td>
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<tr>
<td>$C_3H_7 + M \rightarrow C_2H_4 + CH_3 + M$</td>
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<tr>
<td>$C_3H_7 + C_4H_9 \rightarrow C_4H_{10} + C_3H_6$</td>
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<tr>
<td>$2C_3H_6 \rightarrow C_3H_7 + C_3H_5$</td>
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<td>$C_3H_6 \rightarrow C_3H_5 + H$</td>
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<tr>
<td>$C_3H_6 + H \rightarrow C_3H_5 + H_2$</td>
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<tr>
<td>$C_3H_6 + H \rightarrow C_3H_7$</td>
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<tr>
<td>$C_3H_6 + M \rightarrow CH_3 + C_2H_3 + M$</td>
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<td>$C_3H_6 + CH_3 \rightarrow C_4H_9$</td>
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<td>$C_3H_6 + C_4H_9 \rightarrow C_4H_{10} + C_3H_5$</td>
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<td>$C_3H_5 + H_2 \rightarrow C_3H_6 + H$</td>
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<td>$C_3H_5 \rightarrow CH_2 + C_3H_5$</td>
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<td>$C_4H_9 + M \rightarrow C_2H_4 + C_2H_5 + M$</td>
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<td>Reaction</td>
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</tr>
<tr>
<td>$C_4H_9 + CH_2 \rightarrow C_2H_4 + C_3H_7$</td>
</tr>
<tr>
<td>$C_4H_9 \rightarrow C_3H_6 + CH_3$</td>
</tr>
<tr>
<td>$C_4H_9 + H_2 \rightarrow C_4H_{10} + H$</td>
</tr>
<tr>
<td>$C_4H_{10} + CH_3 \rightarrow CH_4 + C_4H_9$</td>
</tr>
<tr>
<td>$C_4H_{10} + M \rightarrow C_3H_7 + CH_3 + M$</td>
</tr>
<tr>
<td>$C_4H_{10} + M \rightarrow 2C_2H_5 + M$</td>
</tr>
<tr>
<td>$C_4H_{10} + H \rightarrow C_4H_9 + H_2$</td>
</tr>
<tr>
<td>$C_4H_{10} + CH_2 \rightarrow C_4H_9 + CH_3$</td>
</tr>
<tr>
<td>$C_4H_{10} + C_2H_3 \rightarrow C_2H_4 + C_4H_9$</td>
</tr>
<tr>
<td>$C_4H_{10} + C_3H_7 \rightarrow C_3H_8 + C_4H_9$</td>
</tr>
<tr>
<td>$C_4H_{10} + C_2H \rightarrow C_2H_2 + C_4H_9$</td>
</tr>
<tr>
<td>$C_4H_{10} + C_2H_5 \rightarrow C_2H_6 + C_4H_9$</td>
</tr>
<tr>
<td>$C_4H_{10} + C_3H_5 \rightarrow C_3H_6 + C_4H_9$</td>
</tr>
<tr>
<td>$C_4H_{10} + CH_2 \rightarrow C_5H_{12}$</td>
</tr>
<tr>
<td>$C_5H_{12} \rightarrow CH_3 + C_4H_9$</td>
</tr>
<tr>
<td>$H_2 + M \rightarrow 2H + M$</td>
</tr>
<tr>
<td>$H_2 + H \rightarrow 3H$</td>
</tr>
<tr>
<td>$2H + M \rightarrow H_2 + M$</td>
</tr>
</tbody>
</table>

### 1.5 Extra reactions included for CH₄-N₂ mixtures in the GAP

For studying the chemistry in a gliding arc plasmatron (GAP) we extended the chemistry set with pure N₂ and CH₄-N₂ chemistry. The pure N₂ reactions are adopted from Ramakers et al. and the coupling reactions are listed below in Table S.5.
Table S.5: Neutral-neutral reactions, as well as the references where the data are adopted from. The rate coefficients are given in cm$^3$ s$^{-1}$ and cm$^6$ s$^{-1}$, for two-body and three-body reactions, respectively. $T_{gas}$ is given in K. $R$ is the gas constant (8.314x10$^{-3}$ kJ mol$^{-1}$ K$^{-1}$). The $\alpha$ parameter determines the effectiveness of lowering the activation energy for reactions involving vibrationally excited levels of the molecules (see details in 46).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Ref</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N + H + M \rightarrow NH + M$</td>
<td>$5.02 \times 10^{-32}$</td>
<td>109</td>
<td></td>
</tr>
<tr>
<td>$N + H_2 \rightarrow NH + H$</td>
<td>$4.65 \times 10^{-10} \exp \left( -\frac{138}{RT_{gas}} \right)$</td>
<td>110</td>
<td>$\alpha = 1.0$</td>
</tr>
<tr>
<td>$N_2 + H \rightarrow NH + N$</td>
<td>$5.27 \times 10^{-10} \frac{T_{gas}^{0.50}}{298} \exp \left( -\frac{619}{RT_{gas}} \right)$</td>
<td>111</td>
<td>$\alpha = 1.0$</td>
</tr>
<tr>
<td>$NH + M \rightarrow N + H + M$</td>
<td>$2.99 \times 10^{-10} \exp \left( -\frac{313}{RT_{gas}} \right)$</td>
<td>112</td>
<td></td>
</tr>
<tr>
<td>$NH + N \rightarrow N_2 + H$</td>
<td>$1.95 \times 10^{-11} \frac{T_{gas}^{0.51}}{298} \exp \left( -\frac{0.08}{RT_{gas}} \right)$</td>
<td>111</td>
<td></td>
</tr>
<tr>
<td>$NH + H \rightarrow H_2 + N$</td>
<td>$1.69 \times 10^{-11}$</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>$NH + H_2 \rightarrow H + NH_2$</td>
<td>$3.50 \times 10^{-11} \exp \left( -\frac{64.50}{RT_{gas}} \right)$</td>
<td>113</td>
<td>$\alpha = 0.5$</td>
</tr>
<tr>
<td>$NH + NH \rightarrow NH_2 + N$</td>
<td>$3.74 \times 10^{-15} \frac{T_{gas}^{3.88}}{298} \exp \left( -\frac{1.43}{RT_{gas}} \right)$</td>
<td>114</td>
<td></td>
</tr>
<tr>
<td>$NH_2 + M \rightarrow H + NH + M$</td>
<td>$1.99 \times 10^{-9} \exp \left( -\frac{318}{RT_{gas}} \right)$</td>
<td>112</td>
<td></td>
</tr>
<tr>
<td>$NH_2 + NH \rightarrow NH_3 + N$</td>
<td>$1.94 \times 10^{-14} \frac{T_{gas}^{2.46}}{298} \exp \left( -\frac{0.45}{RT_{gas}} \right)$</td>
<td>114</td>
<td></td>
</tr>
<tr>
<td>$NH_2 + NH_2 \rightarrow NH_3 + NH$</td>
<td>$8.30 \times 10^{-11} \exp \left( -\frac{41.82}{RT_{gas}} \right)$</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>$NH_2 + N \rightarrow NH + NH$</td>
<td>$2.99 \times 10^{-13} \exp \left( -\frac{63.19}{RT_{gas}} \right)$</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>$NH_2 + H + M \rightarrow NH_3 + M$</td>
<td>$3.01 \times 10^{-30}$</td>
<td>116</td>
<td></td>
</tr>
<tr>
<td>$NH_2 + H \rightarrow NH + H_2$</td>
<td>$1.00 \times 10^{-11}$</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>Pre-exponential</td>
<td>Activation Energy</td>
<td>Frequency Factor</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------</td>
<td>-------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>$NH_2 + H_2 \rightarrow NH_3 + H$</td>
<td>$1.76 \times 10^{-13}$</td>
<td>$12.23 \exp \left( - \frac{30.02}{RT_{gas}} \right)$</td>
<td>117</td>
</tr>
<tr>
<td>$NH_3 + M \rightarrow NH_2 + H + M$</td>
<td>$3.65 \times 10^{-8}$</td>
<td>$391 \exp \left( - \frac{391}{RT_{gas}} \right)$</td>
<td>115</td>
</tr>
<tr>
<td>$NH_3 + M \rightarrow NH + H_2 + M$</td>
<td>$1.05 \times 10^{-9}$</td>
<td>$391 \exp \left( - \frac{391}{RT_{gas}} \right)$</td>
<td>118</td>
</tr>
<tr>
<td>$NH_3 + H \rightarrow NH_2 + H_2$</td>
<td>$7.80 \times 10^{-13}$</td>
<td>$240 \exp \left( - \frac{41.49}{RT_{gas}} \right)$</td>
<td>119</td>
</tr>
<tr>
<td>$NH_3 + NH \rightarrow NH_2 + NH_2$</td>
<td>$2.33 \times 10^{-14}$</td>
<td>$3.41 \exp \left( - \frac{61.11}{RT_{gas}} \right)$</td>
<td>114</td>
</tr>
<tr>
<td>$NH_3 + NH_2 \rightarrow NH_2 + NH_3$</td>
<td>$6.49 \times 10^{-15}$</td>
<td>$2.86 \exp \left( - \frac{38.50}{RT_{gas}} \right)$</td>
<td>117</td>
</tr>
<tr>
<td>$C + NH_2 \rightarrow CH + NH$</td>
<td>$9.61 \times 10^{-13}$</td>
<td>$0.65 \exp \left( - \frac{87.30}{RT_{gas}} \right)$</td>
<td>120</td>
</tr>
<tr>
<td>$CH + N \rightarrow C + NH$</td>
<td>$3.02 \times 10^{-11}$</td>
<td>$0.99 \exp \left( - \frac{10.06}{RT_{gas}} \right)$</td>
<td>121</td>
</tr>
<tr>
<td>$CH + N \rightarrow CN + H$</td>
<td>$1.66 \times 10^{-10}$</td>
<td>$-0.09 \exp \left( - \frac{170}{RT_{gas}} \right)$</td>
<td>121</td>
</tr>
<tr>
<td>$CH_2 + N \rightarrow CH + NH$</td>
<td>$9.96 \times 10^{-13}$</td>
<td>$-0.10 \exp \left( - \frac{170}{RT_{gas}} \right)$</td>
<td>76</td>
</tr>
<tr>
<td>$CH_3 + NH_2 \rightarrow CH_4 + NH$</td>
<td>$2.57 \times 10^{-12}$</td>
<td>$-0.10 \exp \left( - \frac{170}{RT_{gas}} \right)$</td>
<td>122</td>
</tr>
<tr>
<td>$CH_3 + NH_3 \rightarrow CH_4 + NH_2$</td>
<td>$4.95 \times 10^{-14}$</td>
<td>$2.86 \exp \left( - \frac{61.03}{RT_{gas}} \right)$</td>
<td>123</td>
</tr>
<tr>
<td>$CH_4 + NH \rightarrow CH_3 + NH_2$</td>
<td>$4.12 \times 10^{-12}$</td>
<td>$2.86 \exp \left( - \frac{85.08}{RT_{gas}} \right)$</td>
<td>124</td>
</tr>
<tr>
<td>$CH_4 + NH_2 \rightarrow CH_3 + NH_3$</td>
<td>$1.17 \times 10^{-10}$</td>
<td>$71.34 \exp \left( - \frac{71.34}{RT_{gas}} \right)$</td>
<td>125</td>
</tr>
<tr>
<td>$C_2H_6 + NH \rightarrow C_2H_5 + NH_2$</td>
<td>$1.16 \times 10^{-10}$</td>
<td>$70.01 \exp \left( - \frac{70.01}{RT_{gas}} \right)$</td>
<td>126</td>
</tr>
<tr>
<td>$C_2H_6 + NH_2 \rightarrow C_2H_5 + NH_3$</td>
<td>$1.61 \times 10^{-11}$</td>
<td>$47.97 \exp \left( - \frac{47.97}{RT_{gas}} \right)$</td>
<td>127</td>
</tr>
<tr>
<td>$C_3H_8 + NH_2 \rightarrow C_3H_7 + NH_3$</td>
<td>$2.90 \times 10^{-14}$</td>
<td>$3.49 \exp \left( - \frac{26.44}{RT_{gas}} \right)$</td>
<td>128</td>
</tr>
<tr>
<td>$N_2 + H \rightarrow N_2H$</td>
<td>$2.94 \times 10^{-10}$</td>
<td>$0.60 \exp \left( - \frac{64.98}{RT_{gas}} \right)$</td>
<td>111</td>
</tr>
<tr>
<td>$N_2H + M \rightarrow N_2 + H + M$</td>
<td>$2.16 \times 10^{-10}$</td>
<td>$0.11 \exp \left( - \frac{2506.29}{RT_{gas}} \right)$</td>
<td>129</td>
</tr>
</tbody>
</table>
\[
\begin{array}{|c|c|c|}
\hline
\text{reaction} & \text{rate constant} & \text{ref.} \\
\hline
N_2H + H \rightarrow N_2 + H_2 & 8.30 \times 10^{-11} & 47 \\
N_2H + CH_3 \rightarrow CH_4 + N_2 & 4.15 \times 10^{-11} & 47 \\
CN + H_2 \rightarrow HCN + H & 4.90 \times 10^{-19}T_{\text{gas}}^{2.45}\exp \left( - \frac{1127.33}{T_{\text{gas}}} \right) & 130 \alpha = 0.0 \\
HCN + H \rightarrow CN + H_2 & 6.31 \times 10^{-10}\exp \left( - \frac{103}{RT_{\text{gas}}} \right) & 131 \\
CH_3 + N \rightarrow HCN + H_2 & 6.14 \times 10^{-12}T_{\text{gas}}^{0.15}\exp \left( - \frac{45.29}{T_{\text{gas}}} \right) & 129,132 \\
H + CN + M \rightarrow HCN + M & 8.63 \times 10^{-20}\exp \left( - \frac{4.71}{RT_{\text{gas}}} \right) & 133 \\
HCN + M \rightarrow H + CN + M & 1.73 \times 10^5T_{\text{gas}}^{-3.30}\exp \left( - \frac{63714.14}{T_{\text{gas}}} \right) & 47 \\
N_2 + C \rightarrow CN + N & 1.05 \times 10^{-10}\exp \left( - \frac{T_{\text{gas}}}{100} \right) & 134 \alpha = 1.0 \\
n + CN \rightarrow C + N_2 & 3.01 \times 10^{-10} & 54 \\
N_2 + CH \rightarrow HCN + N & 5.18 \times 10^{-15}T_{\text{gas}}^{0.88}\exp \left( - \frac{10130.85}{T_{\text{gas}}} \right) & 47 \alpha = 1.0 \\
N_2 + CH_2 \rightarrow HCN + NH & 1.66 \times 10^{-11}\exp \left( - \frac{37242.07}{T_{\text{gas}}} \right) & 135 \alpha = 1.0 \\
H_2CN + N \rightarrow N_2 + CH_2 & 9.96 \times 10^{-11}\exp \left( - \frac{201.31}{T_{\text{gas}}} \right) & 136 \\
CH_3 + N \rightarrow H_2CN + H & 1.01 \times 10^{-9}T_{\text{gas}}^{-0.31}\exp \left( - \frac{145.95}{T_{\text{gas}}} \right) & 129,132 \\
HCNN + H \rightarrow CH_2 + N_2 & 1.66 \times 10^{-10} & 47 \\
H + HCN \rightarrow H_2CN & k_\infty: 5.50 \times 10^{-11}\exp \left( - \frac{2438}{T_{\text{gas}}} \right) & 137 \\
& k_0: 4.40 \times 10^{-24}T_{\text{gas}}^{-2.73}\exp \left( - \frac{3855}{T_{\text{gas}}} \right) \\
& F_c:(0.95 - 10^{-4})T_{\text{gas}}^{-1} \\
CH + N_2 \rightarrow HCNN & k_\infty: 5.15 \times 10^{-12}T_{\text{gas}}^{0.15}\exp \left( - \frac{372.42}{T_{\text{gas}}} \right) & 47 \alpha = 0.0 \\
& k_0: 3.58 \times 10^{-23}T_{\text{gas}}^{-3.16}\exp \left( - \frac{372.42}{T_{\text{gas}}} \right) \\
& F_c:(1 - 0.667)\exp \left( - \frac{T_{\text{gas}}}{235} \right) + 0.667\exp \left( - \frac{T_{\text{gas}}}{21} \right) \\
N + CH_2 \rightarrow HCN + H & 5.00 \times 10^{-11}\exp \left( - \frac{250}{T_{\text{gas}}} \right) & 138 \\
N + CH_2 \rightarrow CN + H_2 & 1.60 \times 10^{-11} & 139 \\
N + CH_2 \rightarrow CN + H + H & 1.60 \times 10^{-11} & 139,140 \\
CN + CH_4 \rightarrow HCN + CH_3 & 1.00 \times 10^{-11}\exp \left( - \frac{857}{T_{\text{gas}}} \right) & 141 \alpha = 0.0 \\
\hline
\end{array}
\]
1.6 Detailed description of the microdischarges and temperatures used in the DBD model
We assume in our model that the molecules pass a microdischarge every 100 half cycles, based on 150. Indeed, in reality there are more microdischarge filaments in the DBD, but they are spread over the reactor, so not all molecules feel all microdischarges. More details about this approach can be found in 150. In the DBD reactor of Xu and Tu 151, an AC frequency of 20 kHz is applied. Hence, there is a new half cycle every 25 µs. Using the above assumption that the molecules pass a microdischarge every 100 half cycles, the interpulse time is therefore 2.5 ms. As mentioned in the main paper, the power is varied between 15 W and 55 W. Ozkan et al. 152 measured during one AC period in a DBD reactor approximately 400 microdischarges at 50 W and 500 microdischarges at 100 W, with an almost linear increase of the number of discharges as a function of power. Therefore, we assume 330 pulses per AC cycle at 15 W
and 410 pulses per AC cycle at 55 W. The flow rate is varied between 50 and 300 mL min\(^{-1}\), and in combination with the range of plasma power, this corresponds to SEI values between 9 and 54 kJ L\(^{-1}\). The temperature in this DBD configuration was not specified, therefore we estimate the average gas temperature based on the measured electrode temperature in a similar DBD reactor of Ozkan et al.\(^{10}\) albeit used for CO\(_2\) with AC frequency of 28.6 kHz and discharge gap of 2 mm. Ozkan et al.\(^{10}\) reported temperature values varying from 300 K below 30 W towards about 450 K at 100 W in a linear fashion. The authors also presented 2D temperature distributions on the outer electrode, measured by infrared camera, and showed that the aforementioned temperatures at these powers were reached after a travelled distance of 50% of the reactor. Therefore, for power values above 30 W, we let the temperature rise linearly from 300 K at the beginning of the simulation towards the final temperature, i.e. 320 K for 35 W, 340 K for 45 W and 360 K for 55 W. Similar temperatures in the range 300-350 K were also found in a pure CH\(_4\) DBD plasma by Nozaki et al.\(^{153}\).

For the micro-DBD reactor of Wang et al.\(^{154}\) the frequency was not explicitly mentioned, but the same reactor with the same equipment was also used by Duan et al.,\(^{155}\) reporting a range of frequencies of 17.5-19.5 kHz. As this is almost the same as 20 kHz, we also assumed the same interpulse time of 2.5 ms. The power was varied between 10 W and 30 W, and thus we assume 320 pulses per AC cycle at 10 W and 360 pulses per AC cycle at 30 W. The flow rate was varied between 20.2 and 59.8 mL min\(^{-1}\) based on their reported residence times, and we assume the lifetime of the microdischarges to change from 10 ns at 10 W until 12 ns at 30 W. This corresponds to SEI values between 25 and 88 kJ L\(^{-1}\). The wall temperature at 25 W was measured to be 463 K, which is higher than the 300 K assumed in the previous configuration. However, the discharge gap in this configuration, i.e. 0.09 cm, is much smaller, resulting in a higher power density, which heats up the gas more. At lower and higher powers than 25 W, we assume the final temperature to change in the same way as a
function of power, i.e. 10 K with a change of 5 W, as in the work of Ozkan et al. A similar change in temperature was obtained by Nozaki et al. in a pure CH$_4$ DBD plasma, i.e. a temperature increase of 3-10 K for an increase of 5 W.

1.7 Detailed description of the MW model

The inner radius of the discharge tube was 0.3 cm in the configuration of Heintze and Magureanu, and 0.8 cm in the configuration of Shen et al., and the power was deposited over a length of 1 cm and 5.47 cm, respectively, due to a different waveguide design. The power deposition in a MW plasma at reduced pressure is rather uniform in the whole radial direction, and we assume a triangular profile as a function of time, mimicking the axial variation, arising from the waveguide, as done in our previous work. In the setup of Heintze and Magureanu, the power was deposited in either a continuous or pulsed regime. In the continuous regime the plasma power was varied between 20 W and 36 W for a flow rate of 98 sccm, corresponding to SEI values between 12 and 22 kJ L$^{-1}$. In the pulsed regime the average power was ranging between 11 W and 61 W, deposited in pulses between 20 µs and 60 µs, separated by 1 ms. The flow rate was again 98 sccm, corresponding to SEI values between 7 and 37 kJ L$^{-1}$.

In the atmospheric pressure MW reactor of Shen et al., the configuration was optimized in such a way that a homogeneous plasma throughout the entire width of the waveguide was created; hence we assume a uniform power density distribution, instead of a triangular one. At atmospheric pressure, however, we cannot assume a uniform power density in the radial direction, due to radial contraction of the discharge. Moon and Choe reported a plasma radius of 0.27 cm at 600 W, for an inner reactor tube radius of 0.9 cm and a waveguide width of 3.5 cm. Green et al. reported a plasma radius of 0.45 cm at 1400 W, for an inner reactor tube radius of 1.5 cm and a waveguide width of 1.7 cm. These
setups are quite similar to the setup used by Shen et al.\textsuperscript{5}, i.e. inner tube radius of 0.8 cm and a waveguide width of 5.47 cm. Hence, we consider the same plasma radii at these powers, as reported by Moon and Choe\textsuperscript{163} and Green et al.\textsuperscript{164}, and we assume a linear correlation between plasma radius and input power, which results in the same plasma radii in between 900 W and 1400 W as reported by Green et al.\textsuperscript{164}. To apply the model to the experiments of Shen et al.\textsuperscript{5} where plasma powers were varied between 200 W and 800 W, we consider a plasma radius that varies linearly between 0.18 cm and 0.31 cm.

Outside the plasma region, there is still a significant amount of thermal CH\textsubscript{4} conversion. Based on the modelling of Berthelot et al.\textsuperscript{6}, we assume the gas temperature to be more or less constant in the center, within a diameter of 0.8 cm (see red zone in Figure 2 in the main paper). We self-consistently calculated the temperature between 3035 K and 3532 K for the power range between 200 W and 800 W. Similar temperatures were found by Moon and Choe\textsuperscript{163} between 3300 K and 3600 K for powers ranging between 550 W and 700 W. In the region between 0.8 cm and 1.2 cm diameter (blue zone in Figure 2 in the main paper), the gas temperature is taken equal to the average of the gas temperature in the plasma centre (red zone) and room temperature. Between 1.2 cm and 1.6 cm diameter (grey zone in Figure 2 of the main paper), the maximum gas temperature is assumed 300 K lower than in the zone between 0.8 cm and 1.2 cm, as predicted by the modelling of Berthelot et al.\textsuperscript{6}. In our simulations the power is varied between 200 W and 800 W for a flow rate of 500 mL min\textsuperscript{-1} and a CH\textsubscript{4}/H\textsubscript{2} ratio of ¼, corresponding to SEI values between 24 and 96 kJ L\textsuperscript{-1}. In addition, the flow rate is varied between 100 and 1000 mL min\textsuperscript{-1} for the same CH\textsubscript{4}/H\textsubscript{2} ratio of ¼ and a power of 400 W, corresponding to SEI values between 24 and 240 kJ L\textsuperscript{-1}.

1.8 Temperature profile used in the GAP
We assume a temperature profile where the gas in the arc first passes a hot cathode spot with a length of 0.01 cm, as found in Trenchev et al.\textsuperscript{11} with a temperature of 6000 K\textsuperscript{165}, followed
by an instant drop in temperature to 3000 K, which is a typical value inside the arc region outside of the cathode spot $^{11,166,167}$. Next to the arc, there is still a hot zone where the temperature is assumed around 36% of the temperature inside the arc $^{11}$ and where CH$_4$ dissociation can still take place. The temperature profiles are shown in Figure S.1.

![Figure S.1: Temperature profiles as a function of travelled distance inside the GAP for the arc region and outside of the arc.](image)

2. Description of the experiments in the GAP reactor

2.1 Experimental setup

Figure S.2 shows a schematic overview of the experimental setup (left), as well as a schematic picture of GAP reactor (right) with the outer (yellow) and inner (green) vortex gas flows, the plasma arc (purple) and electrodes (black).

The cathode has a length and inner diameter of 10.99 mm and 17.53 mm, respectively. The anode has a length of 16.51 mm and inner diameter of 7.07 mm.
2.1.1 Electrical circuit and plasma power calculation

The main electrical circuit is shown by black lines in Figure S.2. The cathode is connected to the high voltage wire of the power supply (Advanced Plasma Solutions, PA, USA) and the anode is connected to the ground through a resistor.

The plasma power was obtained by measuring the voltage and current passing through the arc, using an oscilloscope (Tektronix TDS2012C) added to the electrical circuit (blue lines). The voltage was measured using a high voltage probe (Testec) connected to the cathode, the ground wire and channel 1 of the oscilloscope. The current was measured using a 6 Ohm resistor in the ground wire, which is connected to channel 2 of the oscilloscope, using $I = V/R$, with $R = 6 \text{ Ohm}$.

The potential and current over a certain period of time were used to calculate the plasma power with the following formula:

$$P_{\text{plasma}} = \frac{1}{T} \int_{0}^{t=T} V_{\text{plasma}} \cdot I_{\text{plasma}} dt$$  \hspace{1cm} (22)

For each condition, we performed six power measurements and took the weighted average for the final power value of each condition.

Figure S.2: Schematic overview of experimental setup (left) and GAP reactor (right).
2.1.2 Gas circuit and detection system
The gas circuit (red lines in Figure S.2), starts from the individual gas bottles of N₂ and CH₄. The flow of every gas is individually regulated by a mass flow controller (MFC) (Bronkhorst), connected to and operated by a computer. The gases mix in the main inlet tube connected to the reactor. The gas mixture enters the reactor through six tangential inlets, each with a diameter of 1.6 mm, giving rise to a vortex flow profile. After passing through the reactor, the gas enters the gas chromatograph (GC) (Thermo Scientific trace 1310 GC) and is stored in sample loops, each with a volume of 100 µL, placed in a valve oven. In order to detect the different components of the gas mixture, a thermal conductivity detector (TCD) is used for the gas analysis. Every gas has its own thermal conductivity, which makes this detector very versatile in the detection of different compounds. The TCD consists of two fixed resistors and two thermal resistors that are arranged in a Wheatstone bridge circuit.

In order to increase the accuracy of the measurements, we performed each experiment three times, and we measured the samples that were stored in four valves, i.e. we averaged over 12 data points for the final result of each condition.

Moreover, we placed two pressure sensors along the gas circuit to monitor the correct working of the setup during the experiments, as well as a temperature probe to monitor the temperature of the outflowing gas of the reactor. The experiments were performed with a total gas flow rate of 10 L min⁻¹ and different fractions of CH₄ in the mixture (i.e., 20, 30, 40, and 50%). For every condition, we measured the CH₄ conversion, based on the GC measurements with and without plasma.

2.1.3 Measurement procedure
Before igniting the plasma, the reactor was flushed for 15 minutes with the gas mixture, to replace the air in the reactor and tubes. The plasma was left to stabilize for 10 minutes before filling the sample loops of the GC. During the filling process, the oscilloscope data was saved six times to obtain the average plasma power for one measurement. The plasma was turned
off and the reactor was left to cool down for the next experiment, while the GC was measuring the sample loops. These results were compared to a blank measurement for which no power was applied and no plasma was created. By comparing the plasma results with those from the blank measurement, we can calculate the gas conversion, as explained below.

2.2 Gas analysis
To obtain the concentration of each molecule \( C_i \) from its peak area \( A_i \) provided by the GC, we first performed a calibration for the compounds to be detected, namely \( \text{CH}_4 \), \( \text{H}_2 \), \( \text{C}_2\text{H}_2 \), \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \), as well as \( \text{N}_2 \) as diluting gas in the gas mixture and \( \text{Ar} \) as internal standard gas (see below).

2.2.1 Correction factor for the gas expansion
\( \text{CH}_4 \) conversion leads to an expansion of gas due to the increasing number of molecules after different reactions inside the plasma (see the reaction list in the modelling section 1 above). As a result, the volumetric flow rate increases. The sample loops in the GC, however, have a constant volume, and therefore gas expansion will result in a pressure rise. However, the GC operates at atmospheric pressure, meaning that part of the gas is lost before injecting in the GC. This results in a lower number of \( \text{CH}_4 \) molecules being detected compared to the number of molecules in the outlet of the reactor, which leads to an overestimation of the conversion. Most papers on plasma-based gas conversion do not account for this expansion factor and therefore report an overestimated conversion.

The expansion factor can be determined by adding an internal standard, such as \( \text{N}_2 \), \( \text{He} \) or \( \text{Ar} \), to the outflow gas stream after the gas has passed through the reactor. \( \text{He} \) cannot be used here, as this is the carrier gas in the GC. \( \text{N}_2 \) is also not possible, because it is introduced in the gas mixture that passes through the GAP reactor. The expansion factor \( \alpha \) is thus obtained by comparing the peak surface area of \( \text{Ar} \) in the chromatogram with and without plasma, assuming that the ratio of the surface areas is proportional with the ratio of the fluxes \(^{169}\).
\[
\alpha = \frac{A_{\text{blank}}}{A_{\text{plasma}}} (1 + \beta) - \beta
\]  

(23)

\( \beta \) is the ratio of the gas flow rate of the internal standard (1 L min\(^{-1}\) in this study) with respect to the total gas flow rate in the GAP (10 L min\(^{-1}\) in this study), i.e., \( \beta = 0.1 \). By adding the internal standard gas, we need to correct the measured concentrations \( (C_m) \) by means of Equation (24) and (25), for the blank and plasma measurements, respectively:

\[
C_{\text{CH}_4}^{\text{blank}} = C_m^{\text{blank}} (1 + \beta)
\]  

(24)

\[
C_{\text{CH}_4}^{\text{plasma}} = C_m^{\text{plasma}} (1 + \beta/\alpha)
\]  

(25)

### 2.2.2 Definition of gas conversion, SEI, EC and selectivity

The CH\(_4\) conversion \( (\chi_{\text{CH}_4}) \) was calculated using Equation (26), in which \( C_{\text{CH}_4}^{\text{blank}} \) and \( C_{\text{CH}_4}^{\text{plasma}} \) are the corrected concentration of CH\(_4\) measured after passing through the GAP without plasma (blank measurement) and with plasma, respectively, and \( \alpha \) is the correction factor for gas expansion defined above.

\[
\chi_{\text{CH}_4}(\%) = \frac{C_{\text{CH}_4}^{\text{blank}} - \alpha \cdot C_{\text{CH}_4}^{\text{plasma}}}{C_{\text{CH}_4}^{\text{blank}}} \cdot 100 \%
\]  

(26)

The specific energy input (SEI) and the energy cost are calculated using Equations (6) to (8) in the main paper. Note that for the experimental SEI, \( P \) is the plasma power calculated from the oscilloscope data (described above) and \( \Phi \) is the total gas flow rate of 10 L min\(^{-1}\).

The C-, and H- based selectivities of the C\(_2\)-based hydrocarbons (C\(_2\)H\(_2\), C\(_2\)H\(_4\), C\(_2\)H\(_6\)), and H\(_2\) are calculated as follows:

\[
S_{C,C_2} = \frac{2\alpha C_{C_2}}{(C_{\text{CH}_4}^{\text{blank}} - \alpha C_{\text{CH}_4}^{\text{plasma}})}
\]  

(27)

\[
S_{H,H_2} = \frac{\alpha C_{H_2}}{2(C_{\text{CH}_4}^{\text{blank}} - \alpha C_{\text{CH}_4}^{\text{plasma}})}
\]  

(28)

Where \( C_{C_2} \) and \( C_{H_2} \) are the concentration of C\(_2\) hydrocarbons and H\(_2\), respectively, known as product yield.
3. Calculation results

3.1 Vibrational temperatures inside the different plasma reactors

Figure S.3: Calculated vibrational temperature and corresponding gas temperature as a function of flow rate, at a plasma power of 45 W in the atmospheric pressure DBD reactor of Xu and Tu.\textsuperscript{151}

Figure S.4: Calculated vibrational temperature and corresponding gas temperature as a function of power, at a flow rate of 100 mL min\textsuperscript{-1} in the atmospheric pressure DBD reactor of Xu and Tu.\textsuperscript{151}
Figure S.5: Calculated vibrational temperature and corresponding gas temperature as a function of flow rate, at a plasma power of 25 W in the atmospheric pressure DBD reactor of Wang et al. 154.

Figure S.6: Calculated vibrational temperature and corresponding gas temperature as a function of power, at a flow rate of 20.24 mL min$^{-1}$ in the atmospheric pressure DBD reactor of Wang et al. 154.
**Figure S.7:** Calculated gas temperature (solid lines) and vibrational temperatures (dashed lines) as a function of travelled distance inside the reduced pressure MW plasma in the continuous regime for different SEI values.

**Figure S.8:** Calculated gas temperature and vibrational temperature as a function of SEI inside the reduced pressure MW plasma in the pulsed regime.
Figure S.9: Calculated gas temperature and vibrational temperature as a function of microwave power, at a flow rate of 500 mL min$^{-1}$ in an atmospheric pressure MW plasma, for a CH$_4$/H$_2$ ratio of $\frac{1}{4}$. The gas and vibrational temperature virtually overlap.

Figure S.10: Calculated gas temperature and vibrational temperature as a function of flow rate, at a microwave power of 400 W in an atmospheric pressure MW plasma, for a CH$_4$/H$_2$ ratio of $\frac{1}{4}$. The gas and vibrational temperature virtually overlap.
Figure S.11: Calculated gas temperature (solid line) and vibrational temperature (dashed line) as a function of travelled distance inside the GAP reactor for different CH$_4$ fractions. The gas and vibrational temperatures virtually overlap.

3.2 Calculated rates of the most important reactions in the different plasma reactors

Table S.6: Calculated rates, averaged over all conditions studied, of the most important reactions in the DBD.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate (cm$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e^- + CH_4 \rightarrow e^- + CH_3 + H$</td>
<td>$1 \times 10^{18}$</td>
</tr>
<tr>
<td>$CH_3 + H + M \rightarrow CH_4 + M$</td>
<td>$1 \times 10^{18}$</td>
</tr>
<tr>
<td>$CH_3 + C_2H_5 + M \rightarrow C_2H_6 + H$</td>
<td>$2 \times 10^{17}$</td>
</tr>
<tr>
<td>$C_2H_4 + H + M \rightarrow C_2H_5 + M$</td>
<td>$2 \times 10^{17}$</td>
</tr>
<tr>
<td>$e^- + CH_4 \rightarrow e^- + CH_2 + H_2$</td>
<td>$1 \times 10^{17}$</td>
</tr>
<tr>
<td>$e^- + C_2H_6 \rightarrow e^- + C_2H_4 + H_2$</td>
<td>$1 \times 10^{17}$</td>
</tr>
<tr>
<td>$CH + CH_4 \rightarrow C_2H_4 + H$</td>
<td>$6 \times 10^{16}$</td>
</tr>
<tr>
<td>$C_2H_5 + H + M \rightarrow C_2H_6 + M$</td>
<td>$6 \times 10^{16}$</td>
</tr>
<tr>
<td>$C_2H_5 + C_2H_5 + M \rightarrow C_4H_{10} + M$</td>
<td>$6 \times 10^{16}$</td>
</tr>
<tr>
<td>$CH_2 + H \rightarrow CH + H_2$</td>
<td>$6 \times 10^{16}$</td>
</tr>
<tr>
<td>$C_2H_5 + H \rightarrow CH_3 + CH_3$</td>
<td>$4 \times 10^{16}$</td>
</tr>
<tr>
<td>$CH_2 + CH_3 \rightarrow C_2H_4 + H$</td>
<td>$3 \times 10^{16}$</td>
</tr>
<tr>
<td>$C_2H_5 + C_2H_5 + M \rightarrow C_3H_8 + M$</td>
<td>$3 \times 10^{16}$</td>
</tr>
<tr>
<td>$e^- + C_2H_5 \rightarrow C_2H_3 + H + H$</td>
<td>$2 \times 10^{16}$</td>
</tr>
<tr>
<td>$CH_3 + C_2H_3 + M \rightarrow C_3H_6 + M$</td>
<td>$2 \times 10^{16}$</td>
</tr>
<tr>
<td>$C_3H_6 + H + M \rightarrow C_3H_7 + M$</td>
<td>$2 \times 10^{16}$</td>
</tr>
<tr>
<td>$C_4H_{10} + CH_2 + M \rightarrow C_5H_{12} + M$</td>
<td>$2 \times 10^{16}$</td>
</tr>
<tr>
<td>$C_3H_7 + H_2 \rightarrow C_3H_8 + H$</td>
<td>$2 \times 10^{16}$</td>
</tr>
<tr>
<td>$e^- + C_2H_4 \rightarrow e^- + C_2H_2 + H_2$</td>
<td>$2 \times 10^{16}$</td>
</tr>
</tbody>
</table>
Table S.7: Calculated rates, averaged over all conditions studied, of the most important reactions in the MW plasma at reduced pressure.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate (cm$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_4 + H \rightarrow \text{CH}_3 + H_2$</td>
<td>$5 \times 10^{-19}$</td>
</tr>
<tr>
<td>$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + H$</td>
<td>$3 \times 10^{-19}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5 + M \rightarrow \text{C}_2\text{H}_4 + H + M$</td>
<td>$1 \times 10^{-19}$</td>
</tr>
<tr>
<td>$\text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3 + \text{CH}_3$</td>
<td>$1 \times 10^{-19}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4 + M \rightarrow \text{C}_2\text{H}_3 + \text{CH}_3 + M$</td>
<td>$1 \times 10^{-19}$</td>
</tr>
<tr>
<td>$\text{e}^- + \text{CH}_4 \rightarrow \text{e}^- + \text{CH}_3 + H$</td>
<td>$9 \times 10^{-18}$</td>
</tr>
<tr>
<td>$\text{CH}_3 + \text{CH}_3 + M \rightarrow \text{C}_2\text{H}_6 + M$</td>
<td>$5 \times 10^{-18}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 + M \rightarrow \text{C}<em>4\text{H}</em>{10} + M$</td>
<td>$8 \times 10^{-17}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_6 + H \rightarrow \text{C}_3\text{H}_5 + H_2$</td>
<td>$7 \times 10^{-17}$</td>
</tr>
<tr>
<td>$\text{e}^- + \text{C}_3\text{H}_6 \rightarrow \text{e}^- + \text{C}_2\text{H}_2 + \text{CH}_4$</td>
<td>$5 \times 10^{-17}$</td>
</tr>
<tr>
<td>$\text{C}<em>4\text{H}</em>{10} + M \rightarrow \text{C}_3\text{H}_7 + \text{CH}_3 + M$</td>
<td>$4 \times 10^{-17}$</td>
</tr>
<tr>
<td>$\text{CH}_3 + \text{C}_2\text{H}_5 \rightarrow \text{C}_3\text{H}_8 + M$</td>
<td>$2 \times 10^{-17}$</td>
</tr>
<tr>
<td>$\text{e}^- + \text{C}_3\text{H}_8 \rightarrow \text{e}^- + \text{C}_2\text{H}_4 + \text{CH}_4$</td>
<td>$2 \times 10^{-17}$</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_7 + M \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3 + M$</td>
<td>$1 \times 10^{-17}$</td>
</tr>
<tr>
<td>$\text{e}^- + \text{C}_3\text{H}_6 \rightarrow \text{e}^- + \text{C}_2\text{H}_6 + H_2$</td>
<td>$1 \times 10^{-17}$</td>
</tr>
<tr>
<td>$\text{e}^- + \text{C}_3\text{H}_6 \rightarrow \text{e}^- + \text{C}_2\text{H}_5 + H$</td>
<td>$1 \times 10^{-17}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_6 + H \rightarrow \text{C}_2\text{H}_5 + H_2$</td>
<td>$5 \times 10^{-16}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4 + H_2 \rightarrow \text{C}_2\text{H}_3 + H$</td>
<td>$5 \times 10^{-16}$</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_8 + H \rightarrow \text{C}_3\text{H}_7 + H_2$</td>
<td>$3 \times 10^{-16}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_3 + \text{CH}_4 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_4$</td>
<td>$8 \times 10^{-15}$</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_8 + H \rightarrow \text{C}_3\text{H}_7 + H_2$</td>
<td>$7 \times 10^{-15}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_2 + H_2 + M \rightarrow \text{C}_2\text{H}_4 + M$</td>
<td>$5 \times 10^{-15}$</td>
</tr>
</tbody>
</table>
Table S.8: Calculated rates, averaged over all conditions studied, of the most important reactions in the MW plasma at atmospheric pressure.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate (cm$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2H_2 + M\rightarrow C_2H + H + M$</td>
<td>2x10$^{20}$</td>
</tr>
<tr>
<td>$C_2H + H_2\rightarrow C_2H_2 + H$</td>
<td>2x10$^{20}$</td>
</tr>
<tr>
<td>$C_2H_3 + H\rightarrow C_2H_2 + H_2$</td>
<td>4x10$^{19}$</td>
</tr>
<tr>
<td>$C_2H_2 + H_2 + M\rightarrow C_2H_4 + M$</td>
<td>3x10$^{19}$</td>
</tr>
<tr>
<td>$C_2H_4 + H\rightarrow C_2H_3 + H_2$</td>
<td>2x10$^{19}$</td>
</tr>
<tr>
<td>$CH_4 + H\rightarrow CH_3 + H_2$</td>
<td>7x10$^{18}$</td>
</tr>
<tr>
<td>$CH_3 + C_2H_4\rightarrow CH_3 + CH_4$</td>
<td>3x10$^{18}$</td>
</tr>
<tr>
<td>$CH_3 + CH_3\rightarrow C_2H_5 + H$</td>
<td>1x10$^{18}$</td>
</tr>
<tr>
<td>$C_2H_5 + M\rightarrow C_2H_4 + H + M$</td>
<td>1x10$^{18}$</td>
</tr>
<tr>
<td>$CH_4 + M\rightarrow CH_3 + H + M$</td>
<td>4x10$^{17}$</td>
</tr>
<tr>
<td>$CH_4 + CH_3\rightarrow C_2H_6 + H$</td>
<td>3x10$^{17}$</td>
</tr>
<tr>
<td>$C_2H_6 + M\rightarrow CH_3 + CH_3 + M$</td>
<td>3x10$^{17}$</td>
</tr>
<tr>
<td>$CH_3 + C_2H_6\rightarrow C_2H_5 + CH_4$</td>
<td>6x10$^{16}$</td>
</tr>
</tbody>
</table>

Table S.9: Calculated rates, averaged over all conditions studied, of the most important reactions in the GAP.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate (cm$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2 + H + M\rightarrow N_2H + M$</td>
<td>4x10$^{21}$</td>
</tr>
<tr>
<td>$N_2H + H\rightarrow N_2 + H_2$</td>
<td>2x10$^{21}$</td>
</tr>
<tr>
<td>$C_2H_2 + M\rightarrow C_2H + H + M$</td>
<td>1x10$^{21}$</td>
</tr>
<tr>
<td>$C_2H + H_2\rightarrow C_2H_2 + H$</td>
<td>1x10$^{21}$</td>
</tr>
<tr>
<td>$CH_4 + H\rightarrow CH_3 + H_2$</td>
<td>2x10$^{20}$</td>
</tr>
<tr>
<td>$CH_4 + M\rightarrow CH_3 + H + M$</td>
<td>9x10$^{19}$</td>
</tr>
<tr>
<td>$C_2H_4 + H\rightarrow C_2H_3 + H_2$</td>
<td>7x10$^{19}$</td>
</tr>
<tr>
<td>$C_2H_3 + H\rightarrow C_2H_2 + H_2$</td>
<td>3x10$^{19}$</td>
</tr>
<tr>
<td>$C_2H_4 + M\rightarrow C_2H_3 + H + M$</td>
<td>2x10$^{19}$</td>
</tr>
<tr>
<td>$CH_3 + CH_3\rightarrow C_2H_5 + H$</td>
<td>2x10$^{19}$</td>
</tr>
<tr>
<td>$C_2H_5 + M\rightarrow C_2H_4 + H + M$</td>
<td>2x10$^{19}$</td>
</tr>
<tr>
<td>$C_2H_2 + H_2 + M\rightarrow C_2H_4 + M$</td>
<td>1x10$^{19}$</td>
</tr>
<tr>
<td>$CH_3 + C_2H_4\rightarrow CH_3 + CH_4$</td>
<td>8x10$^{18}$</td>
</tr>
<tr>
<td>$CH_3 + N_2H\rightarrow CH_4 + N_2$</td>
<td>5x10$^{18}$</td>
</tr>
<tr>
<td>$CH_4 + CH_3\rightarrow C_2H_6 + H$</td>
<td>2x10$^{18}$</td>
</tr>
<tr>
<td>$C_2H_6 + M\rightarrow CH_3 + CH_3 + M$</td>
<td>3x10$^{17}$</td>
</tr>
<tr>
<td>$CH_2 + C_2H_6\rightarrow C_2H_5 + CH_3$</td>
<td>7x10$^{17}$</td>
</tr>
<tr>
<td>$CH_3 + C_2H_5\rightarrow C_2H_4 + CH_4$</td>
<td>7x10$^{16}$</td>
</tr>
</tbody>
</table>
### 3.3 Plasma effect vs. thermal effect

**Figure S.12:** Net contribution of the most important formation reactions of H, as a function of SEI, in a MW plasma at a pressure of 30 mbar and flow rate of 98 sccm, operating in a continuous (a) and pulsed (b) regime.

**Figure S.13:** Net contribution of the most important formation reactions of CH₃, as a function of SEI, in a MW plasma at a pressure of 30 mbar and flow rate of 98 sccm, operating in a continuous (a) and pulsed (b) regime.

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