

Kinetic Study of Non-Equilibrium Plasma-Assisted Methane Steam Reforming

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Supporting Information

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Appendix A:

Electron-impact reactions and rate constants¹

| no. | reactions | Threshold | A_r | β_r | E_r |
|-----|--|-----------|----------|-----------|----------|
| 1 | $E + CH_4 \Rightarrow E + CH_4$ | 0.162 | 5.08E-07 | -2.82E-01 | 5.97E+04 |
| 2 | $E + CH_4 \Rightarrow E + CH_4$ | 0.361 | 1.26E-04 | -7.45E-01 | 8.56E+04 |
| 3 | $E + CH_4 \Rightarrow E + CH_3 + H$ | 9.00 | 2.29E-04 | -7.17E-01 | 2.95E+05 |
| 4 | $E + CH_4 \Rightarrow E + CH_2 + H_2$ | 10.00 | 3.47E-03 | -9.59E-01 | 3.44E+05 |
| 5 | $E + CH_4 \Rightarrow E + CH + H_2 + H$ | 11.00 | 6.67E-06 | -4.83E-01 | 3.05E+05 |
| 6 | $E + CH_4 \Rightarrow E + C + 2H_2$ | 12.00 | 1.90E-05 | -5.78E-01 | 3.35E+05 |
| 7 | $E + H_2O \Rightarrow E + H_2O$ | 0.206 | 1.01E-08 | -6.71E-01 | 4.73E+03 |
| 8 | $E + H_2O \Rightarrow E + H_2O$ | 0.459 | 6.65E-09 | 8.19E-02 | 2.20E+04 |
| 9 | $E + H_2O \Rightarrow E + H_2O$ | 1.058 | 1.04E-08 | -6.37E-02 | 4.86E+04 |
| 10 | $E + H_2O \Rightarrow E + H_2O$ | 8.445 | 2.42E-07 | -1.76E-01 | 2.43E+05 |
| 11 | $E + H_2O \Rightarrow E + H_2O$ | 14.052 | 5.98E-07 | -2.22E-01 | 4.35E+05 |
| 12 | $E + H_2O \Rightarrow E + OH + H$ | 7.00 | 4.29E-09 | 1.20E-01 | 1.91E+05 |
| 13 | $E + H_2O \Rightarrow O + H_2 + E$ | 13.00 | 5.01E-09 | 1.20E-01 | 3.93E+05 |
| 14 | $E + C_2H_6 \Rightarrow CH_3 + CH_3 + E$ | 7.53 | 9.22E-09 | 1.71E-01 | 1.66E+05 |
| 15 | $E + C_2H_6 \Rightarrow C_2H_5 + H + E$ | 10.12 | 1.81E-06 | -1.92E-01 | 2.88E+05 |
| 16 | $E + C_2H_4 \Rightarrow CH_2 + CH_2 + E$ | 7.462 | 1.86E-08 | 5.95E-02 | 1.75E+05 |
| 17 | $E + C_2H_4 \Rightarrow C_2H_3 + H + E$ | 5.00 | 2.46E-10 | 4.95E-01 | 1.24E+05 |
| 18 | $E + C_2H_2 \Rightarrow CH + CH + E$ | 7.902 | 3.34E-06 | -2.77E-01 | 1.67E+05 |
| 19 | $E + C_2H_2 \Rightarrow C_2H + H + E$ | 5.089 | 1.90E-03 | -1.05E+00 | 1.49E+05 |
| 20 | $E + CH_4 \Rightarrow CH_4 + 2E$ | 13.00 | 2.13E-08 | 1.20E-01 | 3.59E+05 |
| 21 | $E + CH_4 \Rightarrow CH_3 + H + 2E$ | 14.3 | 2.20E-08 | 1.20E-01 | 4.08E+05 |
| 22 | $E + CH_4 \Rightarrow CH_3 + H^-$ | 7.7 | 1.60E+01 | -2.35E+00 | 2.52E+05 |
| 23 | $E + CH_4 \Rightarrow CH_2 + H_2$ | 9.00 | 1.35E+01 | -2.39E+00 | 2.90E+05 |
| 24 | $E + H_2O \Rightarrow OH^- + H$ | 3.28 | 6.99E-10 | -3.35E-01 | 9.34E+04 |
| 25 | $E + H_2O \Rightarrow H^- + OH$ | 4.36 | 5.36E-04 | -1.26E+00 | 1.08E+05 |
| 26 | $E + H_2O \Rightarrow H_2 + O^-$ | 3.58 | 3.34E-05 | -1.13E+00 | 1.44E+05 |
| 27 | $E + CH_3 \Rightarrow CH_3 + 2E$ | 10.0 | 8.53E-11 | 5.19E-01 | 1.99E+05 |

¹Reaction rate coefficient $kr = A_r T^{\beta_r} \exp(-E_r/T)$, Units: A_r , cm·molecules·s·K; β_r , dimensionless; E_r , (Ea/R), K.

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|----|--------------------------------------|------|----------|-----------|----------|
| 28 | $E + CH_3 \Rightarrow CH_2 + H + 2E$ | 15.0 | 1.38E-08 | 3.54E-01 | 2.47E+01 |
| 29 | $E + CH_2 \Rightarrow CH_2 + 2E$ | 11.0 | 2.31E-10 | 4.42E-01 | 2.15E+05 |
| 30 | $E + CH \Rightarrow CH + H + 2E$ | 16.0 | 1.72E-10 | 4.00E-01 | 2.99E+05 |
| 31 | $E + CH \Rightarrow CH + 2E$ | 11.0 | 6.16E-10 | 3.65E-01 | 2.30E+05 |
| 32 | $E + CH \Rightarrow C + H + 2E$ | 16.0 | 9.24E-11 | 4.18E-01 | 3.16E+05 |
| 33 | $E + H_2 \Rightarrow H + H + E$ | 8.90 | 9.91E-04 | -9.37E-01 | 2.31E+05 |

Appendix B:

Radical reactions and rate constants

| no. | reactions | A_r | β_r | E_r | no. | reactions | A_r | β_r | E_r |
|-----|--|----------|-----------|--------|-----|---|----------|-----------|---------|
| 34 | $CH_3 + CH_2 \Rightarrow C_2H_4 + H$ | 1.50E-07 | -1.17 | 320.0 | 105 | $C_2H_5 + CH_3OH \Rightarrow C_2H_6 + CH_3O$ | 2.39E-23 | 3.10 | 4500.0 |
| 35 | $CH_3 + H \Rightarrow H_2 + CH_2$ | 7.01E-11 | 0.00 | 0.0 | 106 | $C_2H_5 + CH_3O \Rightarrow C_2H_6 + CH_2O$ | 4.00E-11 | 0.00 | 0.0 |
| 36 | $CH_3 + H \Rightarrow CH_4$ | 1.00E-10 | 0.00 | 7600.0 | 107 | $C_2H_5 + CH_2O \Rightarrow C_2H_6 + HCO$ | 9.14E-21 | 2.81 | 2950.0 |
| 37 | $CH_2 + CH_2 \Rightarrow C_2H_2 + H_2$ | 2.01E-09 | -0.40 | 0.0 | 108 | $C_2H_5 + HCO \Rightarrow C_2H_6 + CO$ | 2.01E-10 | 0.00 | 0.0 |
| 38 | $CH_2 + H \Rightarrow CH + H_2$ | 2.62E-09 | 0.00 | 6010.0 | 109 | $C_2H_5 + O \Rightarrow CH_2O + CH_3$ | 2.67E-11 | 0.00 | 0.0 |
| 39 | $CH_3 + OH \Rightarrow CH_3OH$ | 1.00E-11 | 0.00 | -900.0 | 110 | $C_2H_5 + O \Rightarrow C_2H_4 + OH$ | 6.31E-12 | 0.00 | 0.0 |
| 40 | $CH_2 + OH \Rightarrow CH_2O + H$ | 1.04E-10 | -0.02 | -16.8 | 111 | $C_2H_3 + C_2H_6 \Rightarrow C_2H_4 + C_2H_5$ | 9.99E-22 | 3.30 | 5280.0 |
| 41 | $CH + H \Rightarrow C + H_2$ | 3.01E-11 | 0.00 | 0.0 | 112 | $C_2H_3 + C_2H_3 \Rightarrow C_2H_4 + C_2H_2$ | 1.60E-12 | 0.00 | 0.0 |
| 42 | $CH_3OH + OH \Rightarrow CH_3O + H_2O$ | 1.31E-10 | 0.00 | 80.6 | 113 | $C_2H_3 \Rightarrow C_2H_2 + H$ | 6.81E+17 | -7.49 | 22900.0 |
| 43 | $CH_3OH + CH_2 \Rightarrow CH_3O + CH_3$ | 2.88E-23 | 3.40 | -575.0 | 114 | $C_2H_5 \Rightarrow C_2H_4 + H$ | 3.06E+10 | 0.95 | 18600.0 |
| 44 | $CH_3OH + CH_3 \Rightarrow CH_3O + CH_4$ | 2.39E-23 | 3.10 | 3490.0 | 115 | $C_2H_3 + CH_4 \Rightarrow C_2H_4 + CH_3$ | 2.41E-24 | 4.02 | 2750.0 |
| 45 | $CH_3O + H \Rightarrow CH_3OH$ | 2.39E-23 | 3.10 | 3490.0 | 116 | $C_2H_3 + CH_3 \Rightarrow C_2H_2 + CH_4$ | 1.24E-03 | -3.20 | 0.0 |
| 46 | $CH_3O + OH \Rightarrow CH_2O + H_2O$ | 4.05E-11 | 0.24 | -26.5 | 117 | $C_2H_3 + CH_3 \Rightarrow C_3H_6$ | 1.20E-10 | 0.00 | 0.0 |
| 47 | $CH_3O + CH_3 \Rightarrow CH_2O + CH_4$ | 3.01E-11 | 0.00 | 0.0 | 118 | $C_2H_3 + CH_2 \Rightarrow C_2H_2 + CH_3$ | 3.01E-11 | 0.00 | 0.0 |
| 48 | $CH_3O + CH_4 \Rightarrow CH_3OH + CH_3$ | 4.00E-11 | 0.00 | 0.0 | 119 | $C_2H_3 + CH_3OH \Rightarrow C_2H_4 + CH_3O$ | 2.39E-23 | 3.10 | 3490.0 |
| 49 | $CH_3O + CH_2 \Rightarrow CH_2O + CH_3$ | 2.61E-13 | 0.00 | 4450.0 | 120 | $C_2H_3 + CH_3O \Rightarrow CH_2O + C_2H_4$ | 4.00E-11 | 0.00 | 0.0 |
| 50 | $CH_2O + CH_2 \Rightarrow CH_3 + HCO$ | 3.01E-11 | 0.00 | 0.0 | 121 | $C_2H_3 + CH_2O \Rightarrow C_2H_4 + HCO$ | 6.40E-21 | 2.87 | 2950.0 |
| 51 | $CH_2O + CH_3 \Rightarrow CH_4 + HCO$ | 1.00E-14 | 0.00 | 0.0 | 122 | $C_2H_3 + HCO \Rightarrow C_2H_4 + CO$ | 5.00E-07 | 0.00 | 0.0 |
| 52 | $CH_2O + H \Rightarrow H_2 + HCO$ | 1.29E-31 | 6.10 | 990.0 | 123 | $C_2H_3 + H \Rightarrow C_2H_4$ | 6.46E-11 | 0.20 | 0.0 |
| 53 | $CH_2O + OH \Rightarrow HCO + H_2O$ | 3.79E-14 | 1.05 | 1650.0 | 124 | $C_2H_3 + H \Rightarrow C_2H_2 + H_2$ | 2.01E-11 | 0.00 | 0.0 |
| 54 | $HCO + H \Rightarrow CO + H_2$ | 5.69E-15 | 1.18 | -225.0 | 125 | $C_2H_3 + OH \Rightarrow C_2H_2 + H_2O$ | 5.00E-11 | 0.00 | 0.0 |
| 55 | $HCO + OH \Rightarrow CO + H_2O$ | 1.50E-10 | 0.00 | 0.0 | 126 | $C_2H_3 + O \Rightarrow C_2H_2 + OH$ | 1.76E-12 | 0.20 | -215.0 |

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|----|--|----------|------|---------|-----|--|----------|-------|---------|
| 56 | HCO + CH ₄ => CH ₂ O + CH ₃ | 1.69E-10 | 0.00 | 0.0 | 127 | C ₂ H ₄ + CH ₂ => C ₃ H ₆ | 5.00E-17 | 0.00 | 0.0 |
| 57 | HCO + CH ₃ => CH ₄ + CO | 1.06E-24 | 3.78 | 10700.0 | 128 | C ₂ H ₂ + H => C ₂ H + H ₂ | 1.00E-10 | 0.00 | 11200.0 |
| 58 | HCO + CH ₂ => CO + CH ₃ | 2.01E-10 | 0.00 | 0.0 | 129 | CH ₄ + H => H ₂ + CH ₃ | 6.62E-21 | 3.16 | 4410.0 |
| 59 | HCO + H ₂ O => CH ₂ O + OH | 3.01E-11 | 0.00 | 0.0 | 130 | CH ₄ + OH => CH ₃ + H ₂ O | 1.68E-18 | 2.18 | 1230.0 |
| 60 | O + C ₂ H ₄ => CH ₃ + HCO | 3.86E-16 | 1.35 | 13100.0 | 131 | CH ₄ + CH ₂ => CH ₃ + CH ₃ | 3.01E-19 | 0.00 | 0.0 |
| 61 | O + C ₂ H ₂ => CO + CH ₂ | 2.19E-16 | 1.55 | 215.0 | 132 | CO ₂ + CH ₂ => CH ₂ O + CO | 3.90E-14 | 0.00 | 0.0 |
| 62 | O + CH ₄ => CH ₃ + OH | 6.78E-16 | 1.50 | 850.0 | 133 | CO ₂ + H => CO + OH | 2.51E-10 | 0.00 | 13400.0 |
| 63 | O + CH ₃ => CH ₂ O + H | 1.15E-16 | 1.56 | 4270.0 | 134 | CO + C ₂ H ₄ => C ₂ H ₃ + HCO | 2.51E-10 | 0.00 | 45600.0 |
| 64 | O + CH ₃ => CH ₃ O | 1.40E-09 | 0.00 | 0.0 | 135 | CO + CH ₃ O => CO ₂ + CH ₃ | 2.61E-11 | 0.00 | 5940.0 |
| 65 | O + CH => CO + H | 9.18E-11 | 0.05 | -68.6 | 136 | CO + OH => CO ₂ + H | 1.05E-17 | 1.50 | -250.0 |
| 66 | O + CH => C + OH | 6.59E-11 | 0.00 | 0.0 | 137 | H ₂ + C ₂ H ₅ => C ₂ H ₆ + H | 5.10E-24 | 3.60 | 4250.0 |
| 67 | O + CH ₃ OH => CH ₃ O + OH | 2.52E-11 | 0.00 | 2380.0 | 138 | H ₂ + C ₂ H ₄ => C ₂ H ₅ + H | 1.69E-11 | 0.00 | 34300.0 |
| 68 | O + CH ₃ O => CH ₂ O + OH | 1.66E-11 | 0.00 | 2360.0 | 139 | H ₂ + C ₂ H ₂ => C ₂ H ₄ | 5.00E-13 | 0.00 | 19600.0 |
| 69 | O + CH ₂ O => HCO + OH | 1.00E-11 | 0.00 | 0.0 | 140 | H ₂ + C ₂ H ₂ => C ₂ H ₃ + H | 4.00E-12 | 0.00 | 32700.0 |
| 70 | O + HCO => CO + OH | 6.92E-13 | 0.57 | 1390.0 | 141 | H ₂ + CH ₃ => CH ₄ + H | 1.14E-20 | 2.74 | 4740.0 |
| 71 | O + HCO => CO ₂ + H | 5.00E-11 | 0.00 | 0.0 | 142 | H ₂ + CH ₂ => CH ₃ + H | 5.00E-15 | 0.00 | 0.0 |
| 72 | O + H ₂ O => OH + OH | 4.98E-11 | 0.00 | 0.0 | 143 | H ₂ + CH => CH ₃ | 8.93E-11 | 0.15 | 0.0 |
| 73 | C ₂ H ₆ + H => C ₂ H ₅ + H ₂ | 8.21E-14 | 0.95 | 8570.0 | 144 | H ₂ + CH => CH ₂ + H | 5.51E-16 | 1.79 | 840.0 |
| 74 | C ₂ H ₆ + OH => C ₂ H ₅ + H ₂ O | 5.19E-22 | 3.50 | 2600.0 | 145 | H ₂ + CH ₃ O => CH ₃ OH + H | 2.11E-25 | 4.00 | 2470.0 |
| 75 | C ₂ H ₆ + O => C ₂ H ₅ + OH | 2.74E-18 | 2.22 | 373.0 | 146 | H ₂ + CH ₂ O => CH ₃ OH | 2.28E-11 | 0.00 | 35100.0 |
| 76 | C ₂ H ₆ + CH ₃ => C ₂ H ₅ + CH ₄ | 1.66E-15 | 1.50 | 2920.0 | 147 | H ₂ + HCO => CH ₂ O + H | 3.00E-18 | 2.00 | 8970.0 |
| 77 | C ₂ H ₆ + CH ₂ => C ₂ H ₅ + CH ₃ | 9.12E-25 | 4.00 | 4170.0 | 148 | H ₂ + OH => H ₂ O + H | 3.50E-16 | 1.52 | 1740.0 |
| 78 | C ₂ H ₆ + CH ₃ O => CH ₃ OH + C ₂ H ₅ | 1.07E-11 | 0.00 | 3980.0 | 149 | H ₂ + O => OH + H | 8.52E-20 | 2.67 | 3160.0 |
| 79 | C ₂ H ₆ + HCO => CH ₂ O + C ₂ H ₅ | 4.00E-11 | 0.00 | 3570.0 | 150 | H ₂ O + C ₂ H ₅ => C ₂ H ₆ + OH | 5.64E-18 | 1.44 | 10200.0 |
| 80 | C ₂ H ₆ + CH ₂ => C ₃ H ₈ | 3.74E-24 | 3.74 | 8520.0 | 151 | H ₂ O + C ₂ H ₃ => C ₂ H ₄ + OH | 8.02E-22 | 2.90 | 7480.0 |
| 81 | C ₂ H ₄ + C ₂ H ₂ => C ₂ H ₃ + C ₂ H ₃ | 4.80E-12 | 0.00 | 0.0 | 152 | H ₂ O + CH ₃ => CH ₄ + OH | 8.02E-22 | 2.90 | 7480.0 |
| 82 | C ₂ H ₄ + H => C ₂ H ₅ | 4.00E-11 | 0.00 | 34400.0 | 153 | H ₂ O + CH ₂ => CH ₃ + OH | 1.60E-16 | 0.00 | 0.0 |
| 83 | C ₂ H ₄ + OH => C ₂ H ₃ + H ₂ O | 4.20E-16 | 1.75 | 605.0 | 154 | H ₂ O + CH ₃ O => CH ₃ OH + OH | 5.79E-25 | 3.80 | 5780.0 |
| 84 | C ₂ H ₄ + H => C ₂ H ₃ + H ₂ | 2.61E-20 | 2.75 | 2100.0 | 155 | H ₂ O + H => H ₂ + OH | 7.50E-16 | 1.60 | 9720.0 |
| 85 | C ₂ H ₄ + CH ₃ => CH ₄ + C ₂ H ₃ | 2.20E-18 | 2.53 | 6160.0 | 156 | H + H => H ₂ | 1.80E-30 | -1.00 | 0.0 |
| 86 | C ₂ H ₂ + H => C ₂ H ₃ | 1.10E-23 | 3.70 | 4780.0 | 157 | H + OH => H ₂ O | 4.26E-11 | 0.23 | -57.7 |
| 87 | C ₂ H ₂ + OH => CO + CH ₃ | 9.13E-12 | 0.00 | 1220.0 | 158 | H + OH => H ₂ + O | 8.10E-21 | 2.80 | 1950.0 |
| 88 | CH ₃ + CH ₂ => C ₂ H ₄ + H | 8.04E-28 | 4.00 | -1010.0 | 159 | H + O => OH | 1.30E-29 | -1.00 | 0.0 |
| 89 | C ₂ H ₂ + CH ₃ O => CH ₂ O + C ₂ H ₃ | 1.20E-12 | 0.00 | 4530.0 | 160 | C ₃ H ₈ +H=>N*C ₃ H ₇ +H ₂ | 2.20E-17 | 2.54 | 3400.0 |

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|-----|--|----------|------|---------|--|-----|--|----------|-------|--------|
| 90 | HCO +HCO => CH ₂ O + CO | 3.01E-11 | 0.00 | 0.0 | | 161 | C ₃ H ₈ +H=>I*C ₃ H ₇ +H ₂ | 2.17E-18 | 2.40 | 2250.0 |
| 91 | CH ₃ O => CH ₂ O + H | 9.00E-11 | 0.00 | 6790.0 | | 162 | C3H8+OH=>N*C ₃ H ₇ +H ₂ O | 3.79E-12 | 0.00 | 1310.0 |
| 92 | CH ₂ O => CO + H ₂ | 3.49E-09 | 0.00 | 17600.0 | | 163 | C3H8+OH=> I*C ₃ H ₇ +H ₂ O | 4.83E-15 | 1.00 | 130.0 |
| 93 | CH ₃ OH => CH ₃ O + H | 1.19E+07 | 2.39 | 50200.0 | | 164 | C3H8+O=>N*C ₃ H ₇ +OH | 3.20E-19 | 2.68 | 1870.0 |
| 94 | C ₂ H ₅ + C ₂ H ₅ => C ₂ H ₆ + C ₂ H ₄ | 2.37E-12 | 0.00 | 0.0 | | 165 | C3H8+O=>I*C ₃ H ₇ +OH | 7.93E-20 | 2.71 | 1060.0 |
| 95 | C ₂ H ₅ + C ₂ H ₄ => C ₂ H ₆ + C ₂ H ₃ | 1.05E-21 | 3.13 | 9060.0 | | 166 | N*C ₃ H ₇ +H=>C ₃ H ₆ +H ₂ | 3.01E-11 | 0.00 | 0.0 |
| 96 | C ₂ H ₅ + CH ₄ => C ₂ H ₆ + CH ₃ | 1.43E-25 | 4.14 | 6320.0 | | 167 | I*C ₃ H ₇ +H=>C ₃ H ₆ | 5.99E-12 | 0.00 | 0.0 |
| 97 | C ₂ H ₅ + CH ₃ => CH ₄ + C ₂ H ₄ | 1.63E-12 | 0.00 | 0.0 | | 168 | I*C ₃ H ₇ +H=>C ₃ H ₈ | 3.32E-11 | 0.00 | 0.0 |
| 98 | C ₂ H ₅ + CH ₃ => C ₃ H ₈ | 5.60E-11 | 0.00 | 0.0 | | 169 | N*C ₃ H ₇ +OH=>C ₃ H ₆ +H ₂ O | 4.00E-11 | 0.00 | 0.0 |
| 99 | C ₂ H ₅ + CH ₂ => C ₂ H ₄ + CH ₃ | 3.01E-11 | 0.00 | 0.0 | | 170 | I*C ₃ H ₇ +OH=>C ₃ H ₆ +H ₂ O | 4.00E-11 | 0.00 | 0.0 |
| 100 | C ₂ H ₅ + H => C ₂ H ₆ | 9.04E-11 | 0.16 | 0.0 | | 171 | I*C ₃ H ₇ +CH ₃ =>C ₄ H ₁₀ | 2.26E-09 | -0.68 | 0.0 |
| 101 | C ₂ H ₅ + H => CH ₃ + CH ₃ | 5.99E-11 | 0.00 | 0.0 | | 172 | C ₃ H ₆ +CH ₃ =>C ₄ H ₉ | 3.15E-21 | 2.67 | 3450.0 |
| 102 | C ₂ H ₅ + H => C ₂ H ₄ + H ₂ | 3.01E-11 | 0.00 | 0.0 | | 173 | C ₄ H ₉ +CH ₃ =>C ₅ H ₁₂ | 3.19E-10 | -0.32 | 0.0 |
| 103 | C ₂ H ₅ + OH => C ₂ H ₆ + O | 1.66E-40 | 8.80 | 250.0 | | 174 | C ₃ H ₆ +H=>I*C ₃ H ₇ | 7.06E-13 | 0.51 | 619.0 |
| 104 | C ₂ H ₅ + OH => C ₂ H ₄ + H ₂ O | 4.00E-11 | 0.00 | 0.0 | | 175 | C ₃ H ₆ +H=>N*C ₃ H ₇ | 4.15E-13 | 0.51 | 1320.0 |