**Table 1S.** Anharmonicity matrix for TS1 (cm-1) calculated at the KMLYP/cc-pVTZ level.

|  |  |
| --- | --- |
| 1th row | -78.137 0.159 -3.918 -0.186 -0.362 -4.098 -0.154 -2.594 -0.924 -3.797 -6.156 -4.891 -1.799  -3.372 -1.071 -0.073 0.046 1.894 -0.123 -0.094 -1.925 |
| 2th row | 0.159 -56.973 0.252 -9.025 -11.692 -1.636 -2.218 -0.811 0.549 1.577 -0.644 -0.860 -0.003 0.238 0.330 0.444 0.318 -1.322 0.051 0.096 0.008 |
| 3th row | -3.918 0.252 -10.540 -1.286 -0.416 -1.085 5.232 6.154 -8.068 -2.006 0.744 6.092 -0.103  -0.225 1.806 1.682 -1.453 -25.280 -0.047 0.224 -0.058 |
| 4th row | -0.186 -9.025 -1.286 -7.434 1.301 -1.518 -4.115 -1.512 -2.425 -1.118 -1.110 0.239 -0.219  -1.314 -0.405 -0.272 -0.096 1.338 0.324 0.411 -0.224 |
| 5th row | -0.362 -11.692 -0.416 1.301 -6.626 -1.024 -1.912 -0.131 -1.912 -2.042 -0.711 -0.670 -0.632 1.211 -0.165 -0.031 0.173 0.129 -0.416 -0.864 -0.520 |
| 6th row | -4.098 -1.636 -1.085 -1.518 -1.024 -14.435 -10.699 -4.316 -1.515 13.746 0.509 5.154 5.225 22.177 3.883 2.376 1.676 9.677 -0.834 -0.532 -6.119 |
| 7th row | -0.154 -2.218 5.232 -4.115 -1.912 -10.699 -5.738 -5.693 -1.432 4.757 1.381 0.914 -0.039 1.757 0.242 0.075 -1.134 -6.704 -0.162 1.566 -3.778 |
| 8th row | -2.594 -0.811 6.154 -1.512 -0.131 -4.316 -5.693 -2.157 -2.366 -3.608 -2.128 -0.648 -1.355 15.337 -0.043 -1.993 -0.992 -2.768 -0.467 -0.763 -0.395 |
| 9th row | -0.924 0.549 -8.068 -2.425 -1.912 -1.515 -1.432 -2.366 -1.137 -5.676 -5.369 0.624 1.626  -18.431 3.085 -1.257 -0.129 -0.378 -0.276 -0.668 -1.893 |
| 10th row | -3.797 1.577 -2.006 -1.118 -2.042 13.746 4.757 -3.608 -5.676 -2.748 -8.008 -0.267 2.800 2.076 1.036 -1.266 -0.817 -2.501 0.231 -0.051 -1.517 |
| 11th row | -6.156 -0.644 0.744 -1.110 -0.711 0.509 1.381 -2.128 -5.369 -8.008 -1.904 0.997 2.258 -1.142 -0.518 -0.551 -1.002 -11.767 1.127 0.371 -2.537 |
| 12th row | -4.891 -0.860 6.092 0.239 -0.670 5.154 0.914 -0.648 0.624 -0.267 0.997 -1.486 -4.003 -0.312 -0.895 -0.686 0.076 -0.060 -0.458 -0.633 -0.471 |
| 13th row | -1.799 -0.003 -0.103 -0.219 -0.632 5.225 -0.039 -1.355 1.626 2.800 2.258 -4.003 -0.766 6.148 2.152 -0.620 -0.068 2.263 -2.704 -1.517 2.440 |
| 14th row | -3.372 0.238 -0.225 -1.314 1.211 22.177 1.757 15.337 -18.431 2.076 -1.142 -0.312 6.148 13.550 7.900 -0.187 0.165 1.918 0.779 -0.059 -3.905 |
| 15th row | -1.071 0.330 1.806 -0.405 -0.165 3.883 0.242 -0.043 3.085 1.036 -0.518 -0.895 2.152 7.900 0.359 -0.234 0.016 0.001 0.048 0.056 0.744 |
| 16th row | -0.073 0.444 1.682 -0.272 -0.031 2.376 0.075 -1.993 -1.257 -1.266 -0.551 -0.686 -0.620 -0.187 -0.234 0.004 0.041 -0.668 0.178 0.035 -0.469 |
| 17th row | 0.046 0.318 -1.453 -0.096 0.173 1.676 -1.134 -0.992 -0.129 -0.817 -1.002 0.076 -0.068 0.165 0.016 0.041 -0.080 0.681 -0.186 0.074 -0.705 |
| 18th row | 1.894 -1.322 -25.280 1.338 0.129 9.677 -6.704 -2.768 -0.378 -2.501 -11.767 -0.060 2.263 1.918 0.001 -0.668 0.681 22.085 -1.585 -0.389 -15.145 |
| 19th row | -0.123 0.051 -0.047 0.324 -0.416 -0.834 -0.162 -0.467 -0.276 0.231 1.127 -0.458 -2.704 0.779 0.048 0.178 -0.186 -1.585 0.063 -0.455 -1.007 |
| 20th row | 20 -0.094 0.096 0.224 0.411 -0.864 -0.532 1.566 -0.763 -0.668 -0.051 0.371 -0.633 -1.517  -0.059 0.056 0.035 0.074 -0.389 -0.455 0.155 -0.671 |
| 21th row | -1.925 0.008 -0.058 -0.224 -0.520 -6.119 -3.778 -0.395 -1.893 -1.517 -2.537 -0.471 2.440  -3.905 0.744 -0.469 -0.705 -15.145 -1.007 -0.671 -1.760 |

**Table 2S.** Anharmonicity matrix for TS2 (cm-1) calculated at the KMLYP/cc-pVTZ level.

|  |  |
| --- | --- |
| 1th row | -76.023 0.404 -5.214 -0.561 -1.361 -0.587 -3.954 -0.430 -3.452 -0.464 -2.226 -5.114 -0.894 -0.054 0.005 -0.110 -0.059 -0.140 -0.028 8.506 9.993 |
| 2th row | 0.404 -55.896 -5.772 -8.143 -6.631 -1.392 -4.603 -0.206 -0.167 0.377 -0.659 -0.857 -0.325 0.185 -0.015 0.172 0.010 0.100 -0.012 -0.048 0.841 |
| 3th row | -5.214 -5.772 -4.636 -1.825 14.648 2.995 3.025 -1.334 2.220 0.310 -3.541 -4.171 -0.415 0.711 2.013 1.430 0.978 2.877 0.695 -0.873 -4.363 |
| 4th row | -0.561 -8.143 -1.825 -7.243 1.049 -2.287 -0.611 -2.119 0.128 -2.241 0.464 -3.177 0.007 0.436 -0.130 -0.194 -0.212 -0.054 -0.120 1.140 1.391 |
| 5th row | -1.361 -6.631 14.648 1.049 -2.013 -18.708 17.218 -3.439 -0.690 -3.720 -0.144 11.232 -0.299 -0.461 0.040 -0.583 -0.391 -0.586 0.418 -3.685 5.986 |
| 6th row | -0.587 -1.392 2.995 -2.287 -18.708 -6.802 12.442 -0.425 -2.401 -1.457 -1.382 2.347 -0.503 0.116 -0.662 -1.320 -0.063 -0.565 -0.317 0.462 5.419 |
| 7th row | -3.954 -4.603 3.025 -0.611 17.218 12.442 -14.557 -1.942 7.525 1.916 0.994 -8.931 -1.697 -0.500 1.314 1.954 0.693 1.157 0.280 2.099 -2.400 |
| 8th row | -0.430 -0.206 -1.334 -2.119 -3.439 -0.425 -1.942 -2.044 -1.888 -6.959 -0.596 -1.076 0.115 -1.448 0.811 -0.289 -0.462 -0.461 -0.963 -0.518 -3.492 |
| 9th row | -3.452 -0.167 2.220 0.128 -0.690 -2.401 7.525 -1.888 -2.244 -2.582 -4.017 -0.300 -2.452 -0.709 -0.260 -0.835 -1.107 -0.598 -0.518 -3.421 -1.762 |
| 10th row | -0.464 0.377 0.310 -2.241 -3.720 -1.457 1.916 -6.959 -2.582 -1.994 -1.639 0.734 -0.266 0.539 -1.024 -1.152 -0.091 -0.788 -0.827 -0.980 -0.298 |
| 11th row | -2.226 -0.659 -3.541 0.464 -0.144 -1.382 0.994 -0.596 -4.017 -1.639 -0.941 -9.371 -3.765 -0.308 0.565 0.380 -0.201 0.749 0.177 0.229 3.299 |
| 12th row | -5.114 -0.857 -4.171 -3.177 11.232 2.347 -8.931 -1.076 -0.300 0.734 -9.371 7.533 -0.703 -1.059 -0.762 2.774 -0.645 1.056 -1.214 -1.818 -11.566 |
| 13th row | -0.894 -0.325 -0.415 0.007 -0.299 -0.503 -1.697 0.115 -2.452 -0.266 -3.765 -0.703 -1.062 -0.075 0.076 0.898 -0.626 1.491 -0.219 0.161 -2.413 |
| 14th row | -0.054 0.185 0.711 0.436 -0.461 0.116 -0.500 -1.448 -0.709 0.539 -0.308 -1.059 -0.075 -0.700 -0.346 -0.273 -0.196 -0.112 0.028 -0.437 -0.358 |
| 15th row | 0.005 -0.015 2.013 -0.130 0.040 -0.662 1.314 0.811 -0.260 -1.024 0.565 -0.762 0.076 -0.346 -0.131 -0.060 0.719 -0.279 -0.293 0.483 0.057 |
| 16th row | -0.110 0.172 1.430 -0.194 -0.583 -1.320 1.954 -0.289 -0.835 -1.152 0.380 2.774 0.898 -0.273 -0.060 -0.017 -0.452 -0.107 -0.210 -1.623 -0.894 |
| 17th row | -0.059 0.010 0.978 -0.212 -0.391 -0.063 0.693 -0.462 -1.107 -0.091 -0.201 -0.645 -0.626 -0.196 0.719 -0.452 0.015 0.112 -0.369 -1.209 -1.135 |
| 18th row | -0.140 0.100 2.877 -0.054 -0.586 -0.565 1.157 -0.461 -0.598 -0.788 0.749 1.056 1.491 -0.112 -0.279 -0.107 0.112 0.005 -0.408 -2.565 -0.815 |
| 19th row | -0.028 -0.012 0.695 -0.120 0.418 -0.317 0.280 -0.963 -0.518 -0.827 0.177 -1.214 -0.219 0.028 -0.293 -0.210 -0.369 -0.408 0.092 -1.091 -1.596 |
| 20th row | 8.506 -0.048 -0.873 1.140 -3.685 0.462 2.099 -0.518 -3.421 -0.980 0.229 -1.818 0.161 -0.437 0.483 -1.623 -1.209 -2.565 -1.091 -6.448 -21.083 |
| 21th row | 9.993 0.841 -4.363 1.391 5.986 5.419 -2.400 -3.492 -1.762 -0.298 3.299 -11.566 -2.413 -0.358 0.057 -0.894 -1.135 -0.815 -1.596 -21.083 -5.910 |

**Table 3S.** Anharmonicity matrix for TS3 (cm-1) calculated at the KMLYP/cc-pVTZ level.

|  |  |
| --- | --- |
| 1th row | -76.232 -4.319 -3.257 -0.993 -0.658 0.020 -1.947 -3.136 -3.740 -3.313 -1.430 -1.404 -0.053 -0.222  -0.167 0.027 -0.125 0.126 0.448 15.591 2.989 |
| 2th row | -4.319 -4.237 -6.992 2.993 2.512 -5.989 0.272 -1.309 2.397 6.904 -0.983 -3.468 0.181 2.109  -0.120 0.243 0.131 0.430 0.971 -33.156 7.371 |
| 3th row | -3.257 -6.992 2.413 2.867 -4.613 -4.101 -2.035 1.995 2.090 -0.697 1.639 1.463 -1.484 -0.061  -0.034 0.536 -1.107 0.837 -0.317 37.227 1.410 |
| 4th row | -0.993 2.993 2.867 -5.226 -1.118 -2.470 1.809 0.309 -1.352 -1.420 0.780 0.908 -1.005 0.054  -0.428 -0.167 -1.101 0.319 -1.242 0.890 0.431 |
| 5th row | -0.658 2.512 -4.613 -1.118 -2.521 -2.009 -3.449 -2.948 -0.496 -1.307 -2.326 -1.650 0.115 -1.208  -0.802 0.295 -0.612 -0.276 0.031 -0.434 0.245 |
| 6th row | 0.020 -5.989 -4.101 -2.470 -2.009 -2.262 -2.635 -2.257 -2.532 2.047 2.827 2.985 -0.222 1.359  -0.450 -0.939 0.117 -1.065 -0.202 -4.534 0.276 |
| 7th row | -1.947 0.272 -2.035 1.809 -3.449 -2.635 -2.022 -3.115 -3.722 2.117 0.881 1.917 -0.231 0.565  -0.413 -0.726 -0.693 -0.390 -0.965 -4.549 -1.252 |
| 8th row | -3.136 -1.309 1.995 0.309 -2.948 -2.257 -3.115 -2.051 -4.798 1.546 0.384 4.758 0.605 -0.171 1.276 -1.023 -0.453 -1.415 -0.724 -3.404 -1.547 |
| 9th row | -3.740 2.397 2.090 -1.352 -0.496 -2.532 -3.722 -4.798 -1.053 2.495 -2.042 -1.650 -0.537 -0.254  -0.703 -0.156 -0.470 -0.391 -0.736 -12.353 1.934 |
| 10th row | -3.313 6.904 -0.697 -1.420 -1.307 2.047 2.117 1.546 2.495 -2.049 4.346 2.558 0.137 -1.180  -0.664 -0.426 -0.684 2.573 0.110 6.868 1.256 |
| 11th row | -1.430 -0.983 1.639 0.780 -2.326 2.827 0.881 0.384 -2.042 4.346 2.666 11.435 -1.175 -0.324 0.466 -0.356 -0.184 -1.316 -0.118 -0.547 -1.352 |
| 12th row | -1.404 -3.468 1.463 0.908 -1.650 2.985 1.917 4.758 -1.650 2.558 11.435 1.055 -0.894 0.065 2.441 -0.025 -0.077 -0.455 -0.177 -0.806 -1.578 |
| 13th row | -0.053 0.181 -1.484 -1.005 0.115 -0.222 -0.231 0.605 -0.537 0.137 -1.175 -0.894 -0.089 -0.247  -0.098 -0.210 -0.156 0.027 -0.164 -0.160 -0.138 |
| 14th row | -0.222 2.109 -0.061 0.054 -1.208 1.359 0.565 -0.171 -0.254 -1.180 -0.324 0.065 -0.247 -0.073  -0.230 -0.157 -0.145 0.127 -0.394 1.487 0.062 |
| 15th row | -0.167 -0.120 -0.034 -0.428 -0.802 -0.450 -0.413 1.276 -0.703 -0.664 0.466 2.441 -0.098 -0.230 0.075 0.005 -0.002 -0.286 0.089 -1.543 -0.475 |
| 16th row | 0.027 0.243 0.536 -0.167 0.295 -0.939 -0.726 -1.023 -0.156 -0.426 -0.356 -0.025 -0.210 -0.157 0.005 -0.050 -0.135 -0.084 0.005 0.036 -0.498 |
| 17th row | -0.125 0.131 -1.107 -1.101 -0.612 0.117 -0.693 -0.453 -0.470 -0.684 -0.184 -0.077 -0.156 -0.145  -0.002 -0.135 0.420 0.019 -0.062 -3.947 0.087 |
| 18th row | 0.126 0.430 0.837 0.319 -0.276 -1.065 -0.390 -1.415 -0.391 2.573 -1.316 -0.455 0.027 0.127  -0.286 -0.084 0.019 0.044 0.127 1.834 0.832 |
| 19th row | 0.448 0.971 -0.317 -1.242 0.031 -0.202 -0.965 -0.724 -0.736 0.110 -0.118 -0.177 -0.164 -0.394 0.089 0.005 -0.062 0.127 0.064 -3.192 1.552 |
| 20th row | 15.591 -33.156 37.227 0.890 -0.434 -4.534 -4.549 -3.404 -12.353 6.868 -0.547 -0.806 -0.160 1.487 -1.543 0.036 -3.947 1.834 -3.192 29.841 33.744 |
| 21th row | 2.989 7.371 1.410 0.431 0.245 0.276 -1.252 -1.547 1.934 1.256 -1.352 -1.578 -0.138 0.062  -0.475 -0.498 0.087 0.832 1.552 33.744 1.703 |

**Table 4S**. Fitted parameters for the potential energies and the effective reduced mass for one-dimensional torsions.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Species | Dihedral angle | *V0* |  |  |  |  |  |  |  | φ |
| CHCl2CHCl2 | HCCH | 1733.5 | 865.3 | 594.5 | 1662.6 | 74.0 | 12.9 | -15.1 | 70.0 | 0.0 |
| CH2ClCCl3 | HCCH | 2124.8 | 594.9 | 295.8 | 1958.0 | 37.4 | 0.38 | -1.67 | 6.2 | 0.0 |
| CHCl2CCl3 | HCCH | 3089.8 | -1022.0 | 658.8 | -3070.1 | 59.6 | 7.38 | -4.97 | -23.7 | 0.0 |
| TS1 | ClCCCl | 2827.4 | 303.7 | -642.2 | 2320.4 | 94.1 | 0.17 | -9.9 | 41.3 | 0.0 |
|  | HOHC | -143.9 | 294.1 | -207.7 | 8.2 | 0.869 | 0.0 | 0.0 | 0.0 | 2.03 |
| TS2 | ClCCCl | 2080.0 | 155.2 | 131.6 | 2265.3 | 102.4 | 0.052 | 0.27 | -0.03 | 0.0 |
|  | HOHC | -331.0 | -316.5 | 22.8 | 10.8 | 0.869 | 0.0 | 0.0 | 0.0 | 0.0 |
| TS3 | ClCCCl | -3591.7 | 17.0 | -105.7 | 3339.5 | 142.7 | 0.11 | -0.023 | -0.09 | 0.0 |
|  | HOHC | -263.2 | -229.5 | 10.07 | 0.80 | 0.896 | 0.0 | 0.0 | 0.0 | 0.0 |



**Figure 1S.** The computed rate coefficients for reaction R1 (black circles) in comparison with the plot of suggested equation (dotted line).



**Figure 2S.** The computed rate coefficients for reaction R2 (black circles) in comparison with the plot of suggested equation (dotted line).



**Figure 3S.** The computed rate coefficients for reaction R3 (black circles) in comparison with the plot of suggested equation (dotted line).