

**Table 1S.** Harmonic vibrational wave numbers and moments of inertia  $I_i$  for the reactants and transition states calculated at the KMLYP/cc-pVTZ level.

|                   | The vibrational frequencies ( $\text{cm}^{-1}$ )                                                                                                                                                   | The principle moments of inertia ( $\text{amu } \text{\AA}^2$ ) |
|-------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------|
| 1,1-dibromoethane | 3290.5, 3255.5, 3243.8, 3162.1, 1542.1, 1537.2, 1478.0, 1352.2, 1264.9, 1155.3, 1116.6, 1027.6, 683.6, 590.0, 360.0, 299.3, 271.8, 181.4                                                           | 93.4105<br>401.9731<br>481.6899                                 |
| 1,2-dibromoethane | 3315.2, 3292.4, 3238.5, 3230.1, 1550.1, 1545.1, 1358.3, 1348.8, 1273.2, 1163.0, 1136.1, 996.1, 789.4, 732.3, 657.9, 203.3, 189.1, <u>106.0</u>                                                     | 17.2184<br>829.6746<br>840.6711                                 |
| TS1               | 1720.4i, 3960.6, 3296.4, 3271.6, 3221.9, 1532.6, 1469.9, 1376.2, 1310.9, 1284.6, 1210.7, 1142.7, 1010.7, 887.8, 798.1, 779.4, 681.6, 535.3, 258.3, 209.7, 206.8, 145.7, <u>109.3</u> , <u>93.0</u> | 129.9876<br>834.6366<br>946.6425                                |
| TS1A              | 1717.2i, 3966.1, 3302.7, 3286.5, 3208.8, 1512.0, 1481.5, 1360.5, 1285.8, 1253.4, 1171.6, 1123.3, 1020.6, 897.4, 719.3, 670.2, 591.7, 431.9, 347.5, 231.4, 229.1, 179.4, <u>94.2</u> , <u>65.8</u>  | 210.1314<br>510.6853<br>702.5407                                |
| TS2B              | 1449.4i, 3975.6, 3254.1, 3248.3, 3161.5, 1531.2, 1530.8, 1471.8, 1404.8, 1267.1, 1157.6, 1135.1, 1083., 826.9, 738.8, 661.7, 474.9, 326.4, 291.5, 253.9, 186.5, 138.7, <u>92.0</u> , <u>81.5</u>   | 236.0756<br>467.8620<br>559.7331                                |

**Table 2S.** Anharmonicity matrix for TS1 (cm-1) calculated at the KMLYP/cc-pVTZ level.

|                      |         |         |         |         |         |         |         |         |         |        |        |        |         |
|----------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|--------|--------|--------|---------|
| 1 <sup>th</sup> row  | -78.715 | 0.039   | 0.174   | -0.069  | -0.209  | -2.197  | -1.500  | -1.629  | -1.048  | -0.184 | -0.322 | -1.259 | -10.371 |
|                      | 0.377   | 0.329   | -0.647  | -5.816  | 12.011  | 0.518   | 0.025   | 0.145   |         |        |        |        |         |
| 2 <sup>th</sup> row  | 0.039   | -27.712 | -32.310 | -91.143 | -16.685 | -0.388  | -3.335  | -4.930  | -4.371  | -4.845 | -0.230 | -2.972 | -0.508  |
|                      | -2.814  | 0.170   | 1.745   | 0.166   | -1.226  | 0.280   | 0.231   | 0.101   |         |        |        |        |         |
| 3 <sup>th</sup> row  | 0.174   | -32.310 | -45.880 | -11.414 | -2.231  | 0.380   | -4.353  | -6.389  | -5.291  | -5.118 | -2.336 | -2.213 | -0.235  |
|                      | -2.980  | 0.356   | 0.972   | 0.556   | -0.684  | 0.439   | 0.305   | 0.188   |         |        |        |        |         |
| 4 <sup>th</sup> row  | -0.069  | -91.143 | -11.414 | -29.029 | 4.512   | -0.707  | 0.358   | -0.125  | -3.356  | -4.047 | -1.164 | -3.686 | -0.460  |
|                      | -2.685  | 0.085   | 1.048   | 0.330   | -0.768  | 0.193   | 0.202   | -0.004  |         |        |        |        |         |
| 5 <sup>th</sup> row  | -0.209  | -16.685 | -2.231  | 4.512   | -1.306  | -0.975  | -2.170  | 0.069   | -3.429  | -2.038 | -2.646 | -5.166 | 0.380   |
|                      | -6.227  | -2.013  | -0.477  | 0.403   | -0.325  | -0.186  | 0.308   | -0.434  |         |        |        |        |         |
| 6 <sup>th</sup> row  | -2.197  | -0.388  | 0.380   | -0.707  | -0.975  | -15.350 | -11.732 | -12.473 | -12.905 | -1.960 | 0.406  | 2.246  | -1.565  |
|                      | -4.027  | -0.334  | 3.201   | 29.252  | -33.600 | -3.342  | -2.366  | -0.205  |         |        |        |        |         |
| 7 <sup>th</sup> row  | -1.500  | -3.335  | -4.353  | 0.358   | -2.170  | -11.732 | -4.938  | -1.211  | -1.677  | -6.714 | -2.663 | -0.944 | -2.741  |
|                      | 3.240   | -2.660  | 2.099   | 4.491   | 4.795   | -0.124  | 1.218   | 1.753   |         |        |        |        |         |
| 8 <sup>th</sup> row  | -1.629  | -4.930  | -6.389  | -0.125  | 0.069   | -12.473 | -1.211  | -0.513  | 0.364   | -4.505 | -1.745 | 2.448  | 0.901   |
|                      | 4.597   | -2.892  | -3.342  | 1.231   | 5.691   | 3.809   | 1.315   | 5.158   |         |        |        |        |         |
| 9 <sup>th</sup> row  | -1.048  | -4.371  | -5.291  | -3.356  | -3.429  | -12.905 | -1.677  | 0.364   | -2.477  | -5.546 | -3.675 | 0.454  | 0.818   |
|                      | 0.000   | -2.747  | -2.524  | 1.586   | 12.578  | 3.476   | 2.257   | -0.299  |         |        |        |        |         |
| 10 <sup>th</sup> row | -0.184  | -4.845  | -5.118  | -4.047  | -2.038  | -1.960  | -6.714  | -4.505  | -5.546  | -2.598 | -3.753 | -5.217 | -1.400  |
|                      | 0.688   | -2.059  | -3.985  | -0.945  | -0.373  | -1.118  | -0.777  | -0.750  |         |        |        |        |         |
| 11 <sup>th</sup> row | -0.322  | -0.230  | -2.336  | -1.164  | -2.646  | 0.406   | -2.663  | -1.745  | -3.675  | -3.753 | -5.046 | -3.645 | 0.495   |
|                      | -0.037  | -2.763  | -0.560  | 5.360   | -1.793  | 0.477   | -1.743  | -2.943  |         |        |        |        |         |
| 12 <sup>th</sup> row | -1.259  | -2.972  | -2.213  | -3.686  | -5.166  | 2.246   | -0.944  | 2.448   | 0.454   | -5.217 | -3.645 | -1.296 | -4.374  |
|                      | -0.669  | -2.089  | 2.325   | -3.817  | 3.074   | 1.498   | 6.116   |         |         |        |        |        | 1.060   |
| 13 <sup>th</sup> row | -10.371 | -0.508  | -0.235  | -0.460  | 0.380   | -1.565  | -2.741  | 0.901   | 0.818   | -1.400 | 0.495  | -4.374 | -7.510  |
|                      | -19.978 | 1.199   | 1.294   | 31.565  | 2.197   | -1.516  | -0.843  | -4.197  |         |        |        |        |         |
| 14 <sup>th</sup> row | -0.377  | -2.814  | -2.980  | -2.685  | -6.227  | -4.027  | 3.240   | 4.597   | 0.000   | 0.688  | -0.037 | 1.060  | -19.978 |
|                      | -2.431  | -2.120  | 4.994   | 2.351   | 6.210   | 2.631   | 14.924  |         |         |        |        |        | 4.188   |
| 15 <sup>th</sup> row | 0.329   | 0.170   | 0.356   | 0.085   | -2.013  | -0.334  | -2.660  | -2.892  | -2.747  | -2.059 | -2.763 | -0.669 | 1.199   |
|                      | -2.428  | -7.943  | 1.657   | -1.166  | -1.248  | -0.816  | -3.138  |         |         |        |        |        | -2.431  |
| 16 <sup>th</sup> row | -0.647  | 1.745   | 0.972   | 1.048   | -0.477  | 3.201   | 2.099   | -3.342  | -2.524  | -3.985 | -0.560 | -2.089 | 1.294   |
|                      | -7.943  | -4.383  | 0.834   | 0.878   | -1.451  | -1.237  | -0.146  |         |         |        |        |        | -2.120  |
| 17 <sup>th</sup> row | -5.816  | 0.166   | 0.556   | 0.330   | 0.403   | 29.252  | 4.491   | 1.231   | 1.586   | -0.945 | 5.360  | 2.325  | 31.565  |
|                      | 1.657   | 0.834   | -6.893  | 27.149  | -5.570  | -3.778  | -0.063  |         |         |        |        |        | 4.994   |
| 18 <sup>th</sup> row | 12.011  | -1.226  | -0.684  | -0.768  | -0.325  | -33.600 | 4.795   | 5.691   | 12.578  | -0.373 | -1.793 | -3.817 | 2.197   |
|                      | 2.351   | -1.166  | 0.878   | 27.149  | -60.083 | -2.481  | -2.156  | 1.753   |         |        |        |        |         |
| 19 <sup>th</sup> row | 0.518   | 0.280   | 0.439   | 0.193   | -0.186  | -3.342  | -0.124  | 3.809   | 3.476   | -1.118 | 0.477  | 3.074  | -1.516  |
|                      | -1.248  | -1.451  | -5.570  | -2.481  | -0.094  | -0.152  | 1.015   |         |         |        |        |        | 6.210   |
| 20 <sup>th</sup> row | 0.025   | 0.231   | 0.305   | 0.202   | 0.308   | -2.366  | 1.218   | 1.315   | 2.257   | -0.777 | -1.743 | 1.498  | -0.843  |
|                      | -0.816  | -1.237  | -3.778  | -2.156  | -0.152  | 0.010   | 0.888   |         |         |        |        |        | 2.631   |
| 21 <sup>th</sup> row | 0.145   | 0.101   | 0.188   | -0.004  | -0.434  | -0.205  | 1.753   | 5.158   | -0.299  | -0.750 | -2.943 | 6.116  | -4.197  |
|                      | -3.138  | -0.146  | -0.063  | 1.753   | 1.015   | 0.888   | 0.095   |         |         |        |        |        | 14.924  |

**Table 3S.** Anharmonicity matrix for TS2A (cm-1) calculated at the KMLYP/cc-pVTZ level.

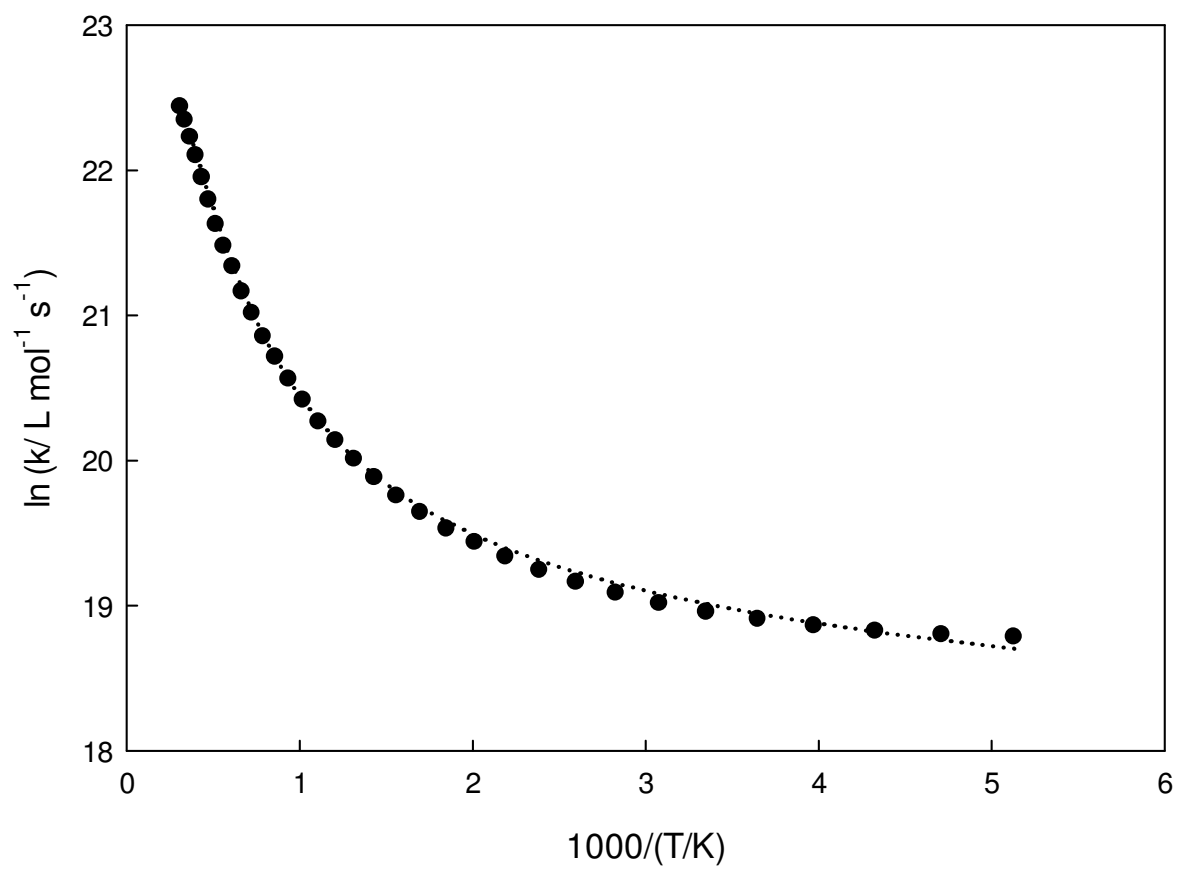
|                      |                   |                   |                  |                   |                   |                  |                  |        |        |         |         |        |         |         |        |
|----------------------|-------------------|-------------------|------------------|-------------------|-------------------|------------------|------------------|--------|--------|---------|---------|--------|---------|---------|--------|
| 1 <sup>th</sup> row  | -77.533<br>-2.034 | 0.340<br>-0.344   | 0.254<br>0.020   | 0.326<br>-0.053   | -0.186<br>3.571   | -3.733<br>-0.456 | -0.710<br>-0.124 | -3.513 | -0.170 | -0.523  | -0.507  | -0.420 | -10.307 | -3.787  |        |
| 2 <sup>th</sup> row  | 0.340<br>-0.435   | -20.649<br>0.354  | -82.149<br>0.173 | -62.748<br>-0.836 | -11.686<br>0.072  | -1.099<br>0.142  | -5.071           | -6.890 | -4.007 | -1.377  | -4.138  | -3.135 | -0.644  | -1.126  | 0.170  |
| 3 <sup>th</sup> row  | 0.254<br>0.677    | -82.149<br>0.392  | -27.747<br>0.272 | -36.826<br>-0.898 | -6.214<br>0.149   | -0.549<br>0.225  | -3.337           | -5.768 | -6.525 | -0.570  | -3.048  | -3.382 | -0.723  | -0.549  | 0.914  |
| 4 <sup>th</sup> row  | 0.326<br>-0.493   | -62.748<br>-0.430 | -36.826<br>0.014 | -28.080<br>-0.170 | 3.222<br>-0.088   | -1.682<br>-0.028 | -2.493<br>0.056  | -3.273 | -0.759 | -1.613  | -5.748  | -3.424 | -0.574  | -1.301  |        |
| 5 <sup>th</sup> row  | -0.186<br>-0.863  | -11.686<br>-0.820 | -6.214<br>-0.655 | 3.222<br>0.409    | -0.743<br>0.920   | -1.785<br>0.030  | -3.392<br>0.059  | -1.390 | -0.459 | -5.915  | -1.531  | -4.214 | -0.019  | 5.316   |        |
| 6 <sup>th</sup> row  | -3.733<br>0.210   | -1.099<br>17.100  | -0.549<br>0.078  | -1.682<br>-17.296 | -1.785<br>0.303   | -5.963<br>0.002  | -3.043           | -8.334 | -0.846 | -1.397  | -0.317  | 1.992  | 1.853   | 14.972  | 0.707  |
| 7 <sup>th</sup> row  | -0.710<br>0.460   | -5.071<br>2.647   | -3.337<br>-0.286 | -2.493<br>3.851   | -3.392<br>0.231   | -3.043<br>-0.213 | -4.858           | -4.183 | 1.007  | -3.960  | 0.359   | -2.670 | 0.477   | 0.581   | 4.006  |
| 8 <sup>th</sup> row  | -3.513<br>0.981   | -6.890<br>22.101  | -5.768<br>1.404  | -3.273<br>14.686  | -1.390<br>3.172   | -8.334<br>-0.347 | -4.183           | 0.858  | 1.751  | -2.021  | 3.492   | 5.032  | -3.055  | 12.966  | 4.801  |
| 9 <sup>th</sup> row  | -0.170<br>0.401   | -4.007<br>-0.692  | -6.525<br>-0.434 | -0.759<br>-1.877  | -0.459<br>-0.257  | -0.846<br>-0.269 | 1.007            | 1.751  | -5.526 | -0.717  | -1.915  | 0.786  | 1.054   | -0.084  | -4.044 |
| 10 <sup>th</sup> row | -0.523<br>-0.678  | -1.377<br>-11.372 | -0.570<br>2.381  | -1.613<br>0.296   | -5.915<br>-4.107  | -1.397<br>-0.555 | -3.960<br>-0.048 | -2.021 | -0.717 | -4.182  | -5.652  | -4.700 | 0.570   | -0.289  |        |
| 11 <sup>th</sup> row | -0.507<br>0.328   | -4.138<br>2.856   | -3.048<br>0.540  | -5.748<br>-10.136 | -1.531<br>2.847   | -0.317<br>0.045  | 0.359            | 3.492  | -1.915 | -5.652  | -3.292  | -0.835 | 4.578   | 0.013   | 2.837  |
| 12 <sup>th</sup> row | -0.420<br>-2.077  | -3.135<br>0.852   | -3.382<br>1.841  | -3.424<br>0.135   | -4.214<br>-2.802  | 1.992<br>2.225   | -2.670<br>-0.280 | 5.032  | 0.786  | -4.700  | -0.835  | -0.299 | -0.692  | -3.558  |        |
| 13 <sup>th</sup> row | -10.307<br>0.111  | -0.644<br>47.224  | -0.723<br>-1.773 | -0.574<br>11.448  | -0.019<br>-2.641  | 1.853<br>-0.214  | 0.477            | -3.055 | 1.054  | 0.570   | 4.578   | -0.692 | -8.243  | 3.512   | 9.480  |
| 14 <sup>th</sup> row | -3.787<br>3.588   | -1.126<br>-64.059 | -0.549<br>-1.328 | -1.301<br>-0.037  | 5.316<br>3.966    | 14.972<br>-0.531 | 0.581            | 12.966 | -0.084 | -0.289  | 0.013   | -3.558 | 3.512   | 11.509  | 13.593 |
| 15 <sup>th</sup> row | -2.034<br>4.876   | 0.170<br>-7.517   | 0.914<br>-0.812  | -0.493<br>2.217   | -0.863<br>-1.905  | 0.707<br>-0.816  | 4.006            | 4.801  | -4.044 | -0.678  | 2.837   | -2.077 | 9.480   | 13.593  | -3.481 |
| 16 <sup>th</sup> row | -0.344<br>-4.876  | -0.435<br>-1.049  | -0.677<br>2.540  | -0.430<br>-0.355  | -0.820<br>-1.325  | -0.210<br>0.560  | -0.460<br>-0.519 | 0.981  | -0.401 | -11.372 | 0.328   | 0.852  | -0.111  | 3.588   |        |
| 17 <sup>th</sup> row | 0.020<br>-7.517   | 0.354<br>2.540    | 0.392<br>7.403   | 0.014<br>2.985    | -0.655<br>-17.773 | 17.100<br>0.026  | 2.647<br>0.144   | 22.101 | -0.692 | 2.381   | 2.856   | 1.841  | 47.224  | -64.059 |        |
| 18 <sup>th</sup> row | -0.053<br>0.355   | 0.173<br>2.985    | 0.272<br>0.254   | -0.170<br>-0.246  | 0.409<br>0.407    | 0.078<br>-0.336  | -0.286           | 1.404  | -0.434 | 0.296   | 0.540   | 0.135  | -1.773  | -1.328  | -0.812 |
| 19 <sup>th</sup> row | 3.571<br>1.325    | -0.836<br>-17.773 | -0.898<br>-0.246 | -0.088<br>-1.325  | 0.920<br>-1.633   | -17.296<br>0.629 | 3.851            | 14.686 | -1.877 | -4.107  | -10.136 | -2.802 | 11.448  | -0.037  | 2.217  |
| 20 <sup>th</sup> row | -0.456<br>0.560   | 0.072<br>0.026    | 0.149<br>0.407   | -0.028<br>-1.633  | 0.030<br>0.024    | 0.303<br>-0.024  | 0.231            | 3.172  | -0.257 | -0.555  | 2.847   | 2.225  | -2.641  | 3.966   | -1.905 |
| 21 <sup>th</sup> row | -0.124<br>0.519   | 0.142<br>0.144    | 0.225<br>-0.336  | 0.056<br>0.629    | 0.059<br>-0.024   | 0.002<br>0.143   | -0.213           | -0.347 | -0.269 | -0.048  | 0.045   | -0.280 | -0.214  | -0.531  | -0.816 |

**Table 4S.** Anharmonicity matrix for TS2B (cm-1) calculated at the KMLYP/cc-pVTZ level.

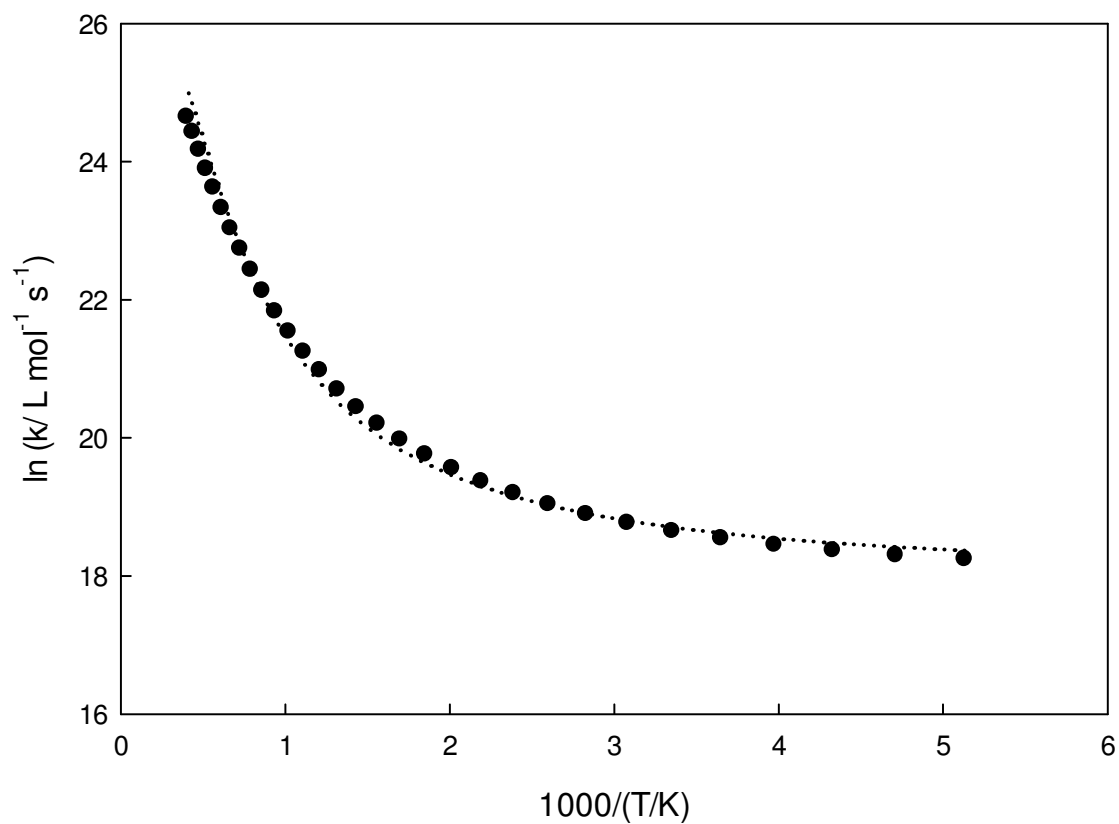
|                      |                                                                                                                                                         |
|----------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1 <sup>th</sup> row  | -76.690 0.043 -0.172 -0.084 -0.077 -0.120 -0.109 -4.790 -5.418 -0.205 -0.372 -0.417 -11.475 -1.647<br>-3.441 -2.653 -1.422 -0.016 -0.308 -0.208 -10.956 |
| 2 <sup>th</sup> row  | 0.043 -29.767 -39.992 -62.527 -16.612 -9.723 -6.478 -0.087 -2.574 0.927 -5.990 -3.909 -0.168 -0.767<br>-0.334 -0.018 -0.311 0.358 -0.221 0.101 -0.650   |
| 3 <sup>th</sup> row  | -0.172 -39.992 -27.572 -73.365 -9.505 -16.597 -7.248 -0.842 -0.700 -4.418 -4.915 -1.118 -0.525 -0.479<br>-0.147 0.992 0.495 -0.799 -1.263 0.053 -0.291  |
| 4 <sup>th</sup> row  | -0.084 -62.527 -73.365 -16.295 2.486 2.681 16.106 -0.438 -1.425 -2.667 -4.081 -2.109 -0.325 -0.396<br>-0.136 0.483 0.192 -0.340 -0.883 0.073 -0.302     |
| 5 <sup>th</sup> row  | -0.077 -16.612 -9.505 2.486 -2.421 -4.081 -4.421 -0.859 0.027 -2.687 -5.313 -2.369 -0.719 -1.070<br>-0.758 -0.040 0.721 0.389 0.518 -0.349 -0.308       |
| 6 <sup>th</sup> row  | -0.120 -9.723 -16.597 2.681 -4.081 -2.281 -5.167 -1.044 -0.296 -3.151 -5.425 -2.286 -1.187 -1.075<br>-0.596 -0.086 0.719 -0.627 -3.261 -0.417 -0.390    |
| 7 <sup>th</sup> row  | -0.109 -6.478 -7.248 16.106 -4.421 -5.167 -9.586 -0.464 -2.145 -5.718 -3.839 -3.917 -0.818 0.159<br>-0.829 0.039 0.243 0.336 0.494 0.086 -0.296         |
| 8 <sup>th</sup> row  | -4.790 -0.087 -0.842 -0.438 -0.859 -1.044 -0.464 2.991 -34.382 0.594 1.361 3.236 -11.174 -6.468<br>2.800 -9.254 -3.007 -0.472 -0.546 -1.844 -30.684     |
| 9 <sup>th</sup> row  | -5.418 -2.574 -0.700 -1.425 0.027 -0.296 -2.145 -34.382 -32.486 2.998 -3.516 -23.865 29.225 23.252<br>9.857 80.012 20.747 -0.709 0.263 3.167 -1.868     |
| 10 <sup>th</sup> row | -0.205 0.927 -4.418 -2.667 -2.687 -3.151 -5.718 0.594 2.998 -3.365 -2.043 -2.252 -0.963 -0.236<br>-1.118 -0.235 -0.312 -2.010 0.161 -0.330 -0.387       |
| 11 <sup>th</sup> row | -0.372 -5.990 -4.915 -4.081 -5.313 -5.425 -3.839 1.361 -3.516 -2.043 -1.509 -2.428 0.057 -0.979<br>-0.756 -0.851 -1.242 -0.123 -0.794 -0.363 -3.470     |
| 12 <sup>th</sup> row | -0.417 -3.909 -1.118 -2.109 -2.369 -2.286 -3.917 3.236 -23.865 -2.252 -2.428 -7.521 11.391 5.141<br>-2.474 14.751 4.689 -0.172 3.224 0.607 2.783        |
| 13 <sup>th</sup> row | -11.475 -0.168 -0.525 -0.325 -0.719 -1.187 -0.818 -11.174 29.225 -0.963 0.057 11.391 -11.318 14.774<br>17.604 12.288 10.037 0.315 -1.658 -1.714 -9.989  |
| 14 <sup>th</sup> row | -1.647 -0.767 -0.479 -0.396 -1.070 -1.075 0.159 -6.468 23.252 -0.236 -0.979 5.141 14.774 2.260<br>1.111 16.281 4.633 -1.202 0.715 -1.761 2.879          |
| 15 <sup>th</sup> row | -3.441 -0.334 -0.147 -0.136 -0.758 -0.596 -0.829 2.800 9.857 -1.118 -0.756 -2.474 17.604 1.111<br>-3.711 0.572 -0.382 -0.577 -0.040 -0.511 18.283       |
| 16 <sup>th</sup> row | -2.653 -0.018 0.992 0.483 -0.040 -0.086 0.039 -9.254 80.012 -0.235 -0.851 14.751 12.288 16.281<br>0.572 4.992 25.133 1.155 -0.652 -1.689 6.398          |
| 17 <sup>th</sup> row | -1.422 -0.311 0.495 0.192 0.721 0.719 0.243 -3.007 20.747 -0.312 -1.242 4.689 10.037 4.633<br>-0.382 25.133 1.092 -0.004 1.645 -0.421 1.832             |
| 18 <sup>th</sup> row | -0.016 0.358 -0.799 -0.340 0.389 -0.627 0.336 -0.472 -0.709 -2.010 -0.123 -0.172 0.315 -1.202<br>-0.577 1.155 -0.004 0.217 -7.845 -0.138 0.602          |
| 19 <sup>th</sup> row | -0.308 -0.221 -1.263 -0.883 0.518 -3.261 0.494 -0.546 0.263 0.161 -0.794 3.224 -1.658 0.715<br>-0.040 -0.652 1.645 -7.845 -3.562 -0.081 -4.155          |
| 20 <sup>th</sup> row | -0.208 0.101 0.053 0.073 -0.349 -0.417 0.086 -1.844 3.167 -0.330 -0.363 0.607 -1.714 -1.761<br>-0.511 -1.689 -0.421 -0.138 -0.081 0.046 -6.821          |
| 21 <sup>th</sup> row | -10.956 -0.650 -0.291 -0.302 -0.308 -0.390 -0.296 -30.684 -1.868 -0.387 -3.470 2.783 -9.989 2.879<br>18.283 6.398 1.832 0.602 -4.155 -6.821 -57.811     |

**Table 5S.** Fitted parameters for the potential energies and the effective reduced mass for one-dimensional torsions.

| Species                              | Dihedral angle | $V_0$  | $V_1^E$ | $V_2^E$ | $V_3^E$ | $V_1^S$ | $V_2^S$ | $I_0$ | $I_1^E$ | $I_2^E$ | $I_3^E$ |
|--------------------------------------|----------------|--------|---------|---------|---------|---------|---------|-------|---------|---------|---------|
| CH <sub>2</sub> BrCH <sub>2</sub> Br | BrCCBr         | 2536.4 | -2583.4 | 1483.7  | -1745.7 | 0.0     | 0.0     | 30.44 | 2.26    | -13.14  | 2.80    |
| TS1                                  | BrCCBr         | 2818.0 | -1918.7 | 725.9   | -1799.7 | 0.0     | 0.0     | 50.56 | -2.79   | -10.11  | 2.90    |
|                                      | HOHC           | 669.0  | -398.3  | -189.9  | -40.1   | 0.0     | 0.0     | 0.85  | 0.010   | -0.019  | 0.00    |
| TS2A                                 | BrCCH          | 1862.0 | -665.7  | 212.2   | -1463.8 | 0.0     | 0.0     | 55.66 | -1.83   | -7.77   | -2.77   |
|                                      | HOHC           | 702.6  | -573.3  | -67.9   | -44.1   | 0.0     | 0.0     | 0.85  | 0.013   | -0.009  | 0.00    |
| TS2B                                 | BrCCH          | 661.0  | 7.89    | -127.9  | -688.3  | 0.0     | 0.0     | 3.09  | 0.056   | -0.23   | -0.58   |
|                                      | HOHC           | 274.5  | -205.9  | -65.9   | 0.0     | 87.0    | -54.2   | 0.86  | 0.011   | -0.006  | 0.00    |



**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).