Tutorial for TUMME 2023

Rui Ming Zhang
Xuefei Xu
Tsinghua University
and
Donald G. Truhlar
University of Minnesota

Outline

- Introduction
- Installation
- How to run
- Input file
- Output files
- Others
- Example

Introduction – 1

What is TUMME ?

- TUMME (Tsinghua University Minnesota Master Equation solver) is a computer program for setting up and solving one-dimensional energy-dependent master equations for gas-phase chemical kinetics.
- TUMME can solve for the phenomenological rate constants and the time evolution of energy-bin populations for a gas-phase reaction network involving single or multiple intermediate energy-wells in a (*P*, *T*) ensemble.

What can TUMME do ?

- Construct the transition matrix of a master equation with discrete energy bins
- Calculate rate constants for collisional energy transfer
- Calculate microcanonical reaction rates including anharmonicity, recrossing, and tunneling
- Calculate phenomenological rate constants for a complicated reaction map
- Calculate the time evolution of energy populations
- Characterize the pressure and temperature dependences of chemical kinetics

Introduction – 2

Basic assumptions of TUMME

- Markov random process

  The transition process depends on the current state and has no historical memory.

- RRKM assumption

  The intramolecular vibrational relaxation (IVR) is faster than reaction.

- Bimolecular reagents equilibrated

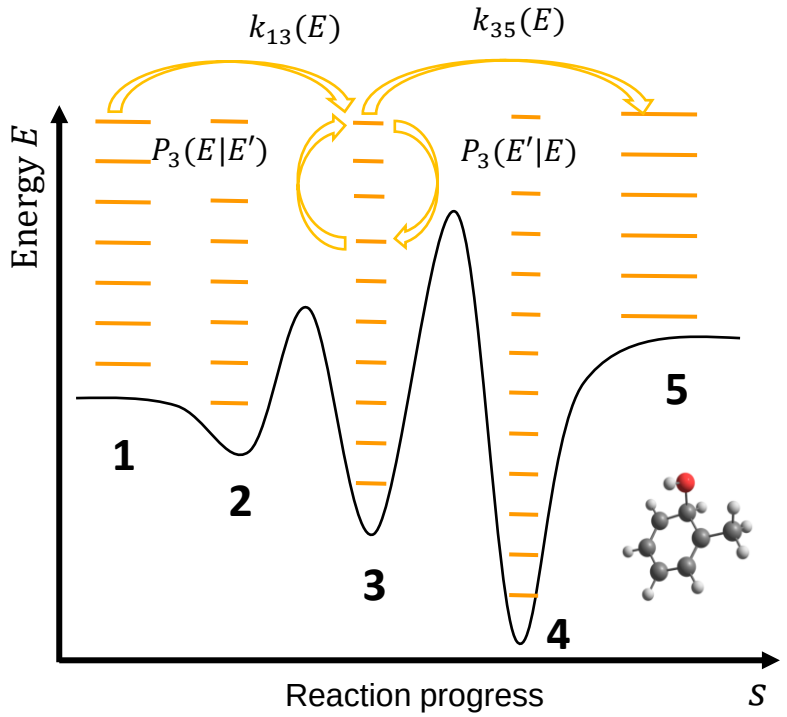
  Bimolecular pairs are always in thermal equilibrium.

- Pressure, temperature, and concentrations

  a) Constant pressure, constant temperature

  b) Bath gas is ideal gas

  c) Bath gas concentration >> reactant and product concentrations



Master equation sketch

Introduction – 3

- Features of TUMME
  - Microcanonical flux coefficients by multistructural variational transition state theory (MS-VTST) with multidimensional tunneling (ZCT, SCT, LCT, or μOMT)
  - Inverse-Laplace transform for microcanonical rate flux coefficients
  - “Exponential-down” collision relaxation mode with energy-dependent $\langle \Delta E_{\mathrm{d}} \rangle$
  - Phenomenological rate constants from chemically significant eigenmodes
  - Pseudo-first order treatment when bimolecular reactions involved
  - MPI and MP parallelism of computer code
  - Double/quadruple/octuple precision for floating-point arithmetic
  - Interfaces available for *Polyrate, MSTor,* and *Gaussian*

Installation

- Installation command:

```
[user@~] tar -Jxvf TUMME2023.xz
[user@~] cd TUMME2023/
[user@~/TUMME2023] ./configure
```

- TUMME is written using Python3.
- To run basic TUMME, Anaconda should be installed.
- To use high-precision libraries, you need the configure file to compile.
- To use MPI, you need to install *mpi4py* module according to this webpage:

https://mpi4py.readthedocs.io/en/stable/install.html#using-pip

```
#!/bin/bash
path=`pwd`
#configure qd must use GNU,     INTEL does NOT work!
cd $path/C++/qd/qd-2.3.7.1
./configure --prefix $path/C++/qd  CXX=g++ CC=gcc FC=gfortran
make clean
make
make install
#compile mini_mpack in dd (quadruple precision)
cd $path/C++/mpack_dd/src
make clean
make
#comile mini_mpack in qd (octuple precision)
cd $path/C++/mpack_qd/src
make clean
make
#compile muti-preicison tumme
cd $path/C++
sed -i "s#^ROOTPATH =.*#ROOTPATH =$path#g" Makefile
make clean
make
#set executble script
cd $path/bin
sed -i "s#^ROOT_PATH=.*#ROOT_PATH=$path#g" tumme
#set enviroment variable
echo "# Enviroment variable of TUMME" >> ~/.bashrc
echo 'export PATH=$PATH:'$path'/bin' >> ~/.bashrc
```

Details in the file configure

How to run

- Run command:

[user@~/TUMME2023] tumme param.in

- The script will run different commands according to the keyword #**PARALLEL** defined in the input file.
- The name of the input file can be any file name.

```
#!/bin/sh
ROOT_PATH=/home/work/TUMME/
SRC_PATH=$ROOT_PATH/src
PYTHON_COMMAND=python3
TUMME_MAIN=tumme_main.py
INPUT=$1
# read parallelism
PARALLEL_STR=$(grep "#parallel" $INPUT|tr -d '\n'|sed -e 's/[ \t]*$//g')
PARALLEL_MODE=$(echo ${PARALLEL_STR##* })
NPROC_STR=$(grep "#nproc" $INPUT|tr -d '\n'|sed -e 's/[ \t]*$//g')
NPROC=$( echo ${NPROC_STR##* })
# omit some check code

# run command
if [ "$PARALLEL_MODE" == "MPI" ]
then
   MPI_COMMAND="mpirun -np "$NPROC
else
   MPI_COMMAND=' '
fi
$MPI_COMMAND $PYTHON_COMMAND $SRC_PATH/$TUMME_MAIN $INPUT
```

Details in the file tumme

Input file – 1

- Structure of the standard input
  - Parallelism keywords
  - Parameter section
  - Reaction section
  - Species section

Structure of the standard input file “param.in”

```
#nproc 4
#parallel mpi
Parameter
    LJCollision
       …
    End_LJCollision
    Edown
      ……
    End_Edown
    Temperature[K]
          ……
    End_Temperature
    Pressure[torr]
          ……
    End_Pressure
    Energy
        ……
    End_Energy
    GroundSpecies     W1
    MergeThreshold    0.5
    Precision         double
    Prints
        ……
    End_Print
End_Parameter
```

```
Reaction
    BarrierRxn
       ……
    End_BarrierRxn

    BarrierlessRxn
       ……
    End_BarrierlessRxn
End_Reaction

Species
    Well
         ……
    End_Well

    TranState
          ……
    End_TranState

    Bim
         ……
    End_Bim

End_Species
```

Input file – 2

Polyrate FU6 file or FU100 file

Gaussian output file

MSTor output file

```
Reaction
    BarrierRxn
        ……
        PLYRate    rxn1.fu100
    End_BarrierRxn

    BarrierlessRxn
        ……
    End_BarrierlessRxn
End_Reaction

Species
    Well
        ……
        G09file    G09W1.log
        MSTfile    mtumme.out
    End_Well

    TranState
        ……
    End_TranState

    Bim
        ……
    End_Bim

End_Species
```

- Interface to external files

Species properties can be read from Polyrate file, Gaussian file, and Species-section, and the priority is

Polyrate file > Gaussian file > Species section

Output files

- *.rate

  Temperature-and-pressure-dependent rate constants and high-pressure limits.

- *.out

  Properties of species and reactions and parameters while solving master equation.

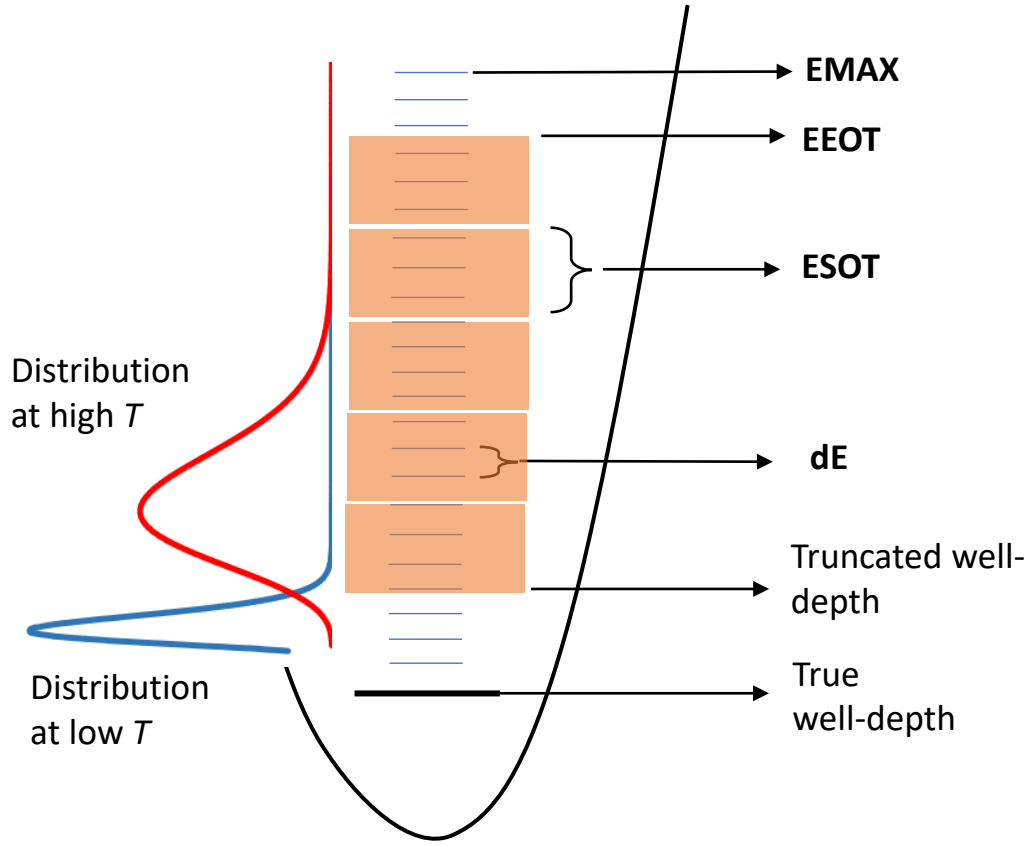
- File printing microcanonical flux coefficients
- File printing partition functions
- File printing collisional energy transfer functions
- File printing time evolution of energetic-bin populations
- File printing CSE eigenvalues
- File printing CSE eigenvectors

  CSE ≡ chemically significant eigenmodes

Other notes – 1

About energy

- Distinguish concepts of **dE**, **ESOT**, **EMAX**, and **EEOT**.
- Ensure **ESOT** > **dE** and **EMAX** > **EEOT.**
- The depth of an isomer well may be truncated due to the numerical method of normalization.
- If some energies of species are read from **E0** or **EELE** and others from **G09file**, one should ensure they have consistent zeros of energy.
- At low temperatures, when molecules mainly populate low energy levels, one should decrease the value of **ESOT**.
- At high temperatures, when molecules populate high energy levels, one should increase the value of **ESOT**.



Other notes – 2

- About symmetry number

Need to define **Rotsigma** when	Not need to define **Rotsigma** when
Read properties from *Polyrate*	Read density of state from *MSTor*
Read properties from **Species** section	Read properties from *Gaussian*

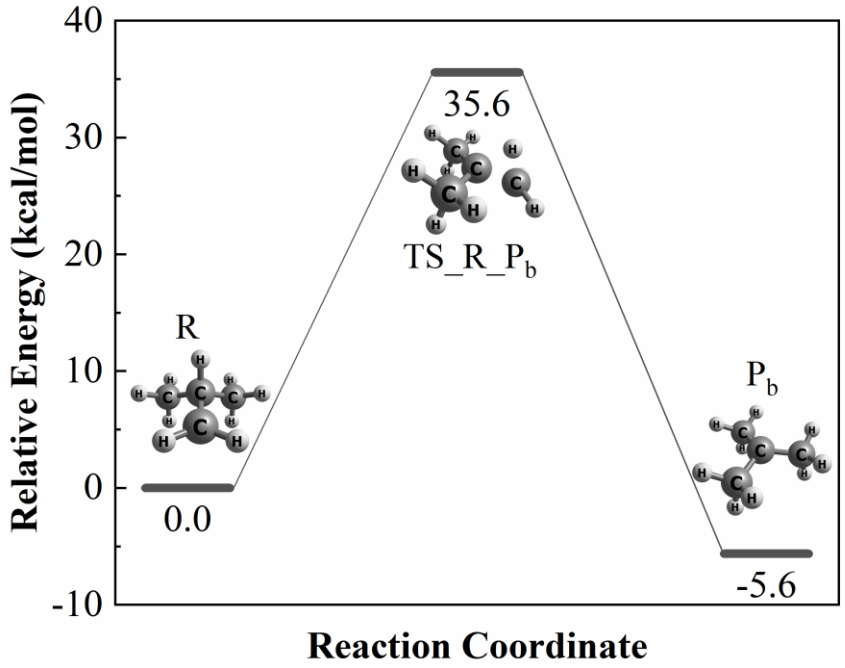
- About frequency scaling factor

Need to define **Freqscale** when	Not need to define **Freqscale** when
Read properties from *Gaussian*	Read density of state from *MSTor*[a]
Read properties from **Species** section	Read properties from *Polyrate*[a]

[a] If, as usual, the frequency scaling has been done in *MSTor* and *Polyrate*.

Example 1

1,2-H-shift isomerization of isobutyl



$$(CH_3)_2CHCH_2\bullet \leftrightarrow (CH_3)_3CH\bullet$$

This is an example for the simplest isomerization reaction. In this example, TST(RRKM) is used with the single-structure-rigid-rotor-harmonic-oscillator approximation. The rate constant and time-evolution of species concentrations are extracted from the master equation

$$\frac{d\mathbf{y}}{dt} = -\mathbf{W}\mathbf{y} \qquad (1)$$

where $\mathbf{y}$ is a vector containing the population of R and P_b, and $\mathbf{W}$ is the transition matrix.

Input: the standard input file
Output: rate constants and the time evolution of concentrations.

Zhang, R. M.; Xu, X.; Truhlar, D. G., *The Journal of Physical Chemistry A* **2021,** *125* (28), 6303-6313.

Example 1 (cont.)

Standard input file

```
#nproc  15
#parallel mp

Parameter
    HSCollision
        Bmax[A]                 9.0
        MassM[amu]              28.0134
    End_HSCollision

    Edown
        EdConst[cm-1]           156.9204
    End_Edown

    Temperature[K]
        1500.
    End_Temperature

    Pressure[torr]
        3E1 7E1 1E2 3E2 7E2 1E3 3E3 7E3 1E4 3E4 7E4 1E5 3E5 7E5 1E6
    End_Pressure

    GroundSpecies           R

    Print
        Timeevolution
            Timefile time.txt
            TimeStep[s] 1E-9
            TimeNum  100
            Initspecies
                R
            END_Initspecies
        END_Timeevolution
    End_Print

End_Parameter

Reaction
    BarrierRxn
        Info  R-TS_R_Pb-Pb
    End_BarrierRxn
End_Reaction
```

Parallelism block

Global parameter block

Collision section

Relaxation section

Temperature

Pressure

Species where zero of energy is placed

Time-evolution

Reaction block

Define the reactant, transition state, and product

Species block

Well/isomer

Geometry

Frequency

Energy

Transition state

```
Species
    Well
        Name R
        Geometry[A]
            C                0.00000500    0.05728400   -0.35846700
            ...
        End_Geometry
        Frequency[cm-1]
            137.0475             235.0936             270.3191
            ...
        End_Frequency
        E0K[a.u.]    -157.628103
    End_Well

    Well
        Name Pb
        Geometry[A]
            C                0.00000000    1.47714300    0.01848500
            ...
        End_Geometry
        Frequency[cm-1]
            132.2029             137.4214             137.4346
            ...
        End_Frequency
        E0K[a.u.]     -157.637096
        Rotsigma   3
    End_Well

    TranState
        Name TS_R_Pb
        Geometry[A]
            C                0.00001700    0.02076500   -0.15960900
            ...
        End_Geometry
        Frequency[cm-1]
            209.6066             217.8881
            ...
        End_Frequency
        E0K[a.u.]    -157.571442
    End_TranState

End_Species
```

Example 1 (cont.)

Standard output file

```
43  ********************** Global Parameter **********************
44    Precision:                  double
45    MergeThreshold:             2.00000E-01
46    GroundSpecies:              R
47    <DeltaE_d>[a.u.]  =  (T/Tc)^(exponent)[ slope*( E - E_gamma,0) + EdConst ]
48      Tc[a.u.]:                 9.50045E-04
49      exponent:                 0.00000E+00
50      slope:                    0.00000E+00
51      EdConst[a.u.]:            7.14982E-04
52    HSCollision
53      bmax[a.u.]:               1.70075E+01
54      massM[a.u.]:              5.10653E+04
55      massA[a.u.]:              None
56
57  ************************** Isomers **************************
58    [MOLECULE PROPERTIES]
59    Name:                       R
60    Read from:                  SPECIES block
61    Number of atoms:            13
62  ›   Geometry [a.u.]:          ···
76    Freuencies scaling factor:  1.00000E+00
77  ›   Frequencies (scaled) [cm-1]:···
87    E(ele) [ a.u.]:             -0.11720102335749813
88    ZPVE  [ a.u.]:              0.11720102335749813
89    E(0K) [ a.u.]:              0.0
90    Eletronic level [a.u.]:
91        1.00000E+00      0.00000E+00
92    Islinear:                   False
93    IABC [a.u.]:                1.11925E+17
94    Symmetry number:            1.00000E+00
95    Optical-isomer number:      1.00000E+00
96    MSTor file:                 None
97    [END OF MOLECULE]
```

Global parameters

Isomer properties

```
187 ********************** Reaction Stack **********************
188 [ REACTION INFO ]
189   Reactant:                   R
190   TS:                         TS_R_Pb
191   Product:                    Pb
192   Polyrate file:              None
193   Variation:                  tst
194   Tunneling:                  None
195   Lower limit of MEP:         None
196   Upper limit of MEP:         None
197   The k(E) will be calculated from the analytical expression.
198 [ END OF INFO ]
199
200 [ REACTION INFO ]
201   Reactant:                   Pb
202   TS:                         TS_R_Pb
203   Product:                    R
204   Polyrate file:              None
205   Variation:                  tst
206   Tunneling:                  None
207   Lower limit of MEP:         None
208   Upper limit of MEP:         None
209   The k(E) will be calculated from the analytical expression.
210 [ END OF INFO ]
211
212 ********************** Reaction Map **********************
213 ( Barrier with ZPVE in a.u.; X denotes none reaction )
214     From/to                   R                 Pb
215 R                             X       5.66610E-02
216 Pb                6.56540E-02                   X
217
218 (  Reaction energy with ZPVE in a.u.; X denotes none reaction )
219     From/to                   R                 Pb
220 R                             X      -8.99300E-03
221 Pb               8.99300E-03                    X
222
```

Elementary reactions

Energies

```
224 ******************** Solve master equation ********************
225
226 ================  Cycle  ================
227
228   Temperature[K]:             1.500E+03
229   Pressure[Torr]:             3.000E+01
230   Energy step[cm-1]:          1.04255E+02
231   Energy reference[cm-1]:     4.37123E+04
232
233 [ RELAXATION INFO ]
234   Name:                       R
235   Size:                       418
236   bmax[a.u.]:                 17.007535
237   Z[1/s]:                     6.389267E+08
238   Truncated well E0[cm-1]:    237.776
239   True well E0:[cm-1]         0.000
240 [ END OF INFO ]
241
242 [ RELAXATION INFO ]
243   Name:                       Pb
244   Size:                       436
245   bmax[a.u.]:                 17.007535
246   Z[1/s]:                     6.389267E+08
247   Truncated well E0[cm-1]:    -1638.820
248   True well E0:[cm-1]         -1973.735
249 [ END OF INFO ]
250
251 [ ME INFO ]
252   Size                        854
253   Min CSE eigenvalue[1/s]:    0.00000E+00
254   Max CSE eigenvalue[1/s]:    4.06206E+05
255   Min IERE eigenvalue[1/s]:   4.84188E+05
256   Max IERE eigenvalue[1/s]:   1.35205E+10
257
258   EPCS:
259     CSE No.                   1             2
260     R                         -3.80037E-01  5.14525E-01
261     Pb                        -9.24971E-01  -2.11400E-01
262
263   Binding:
264     Pb well corresponds to eigen mode 1
265     R well corresponds to eigen mode 2
266
267   Merge Pairs:
268       R -    Pb
269
270 [ END OF INFO ]
```

Parameters for each (*T*, *p*) condition.

Example 1 (cont.)

Rate constants output file

```
48  ********************* Rate constants map *********************
49  *   The diagonal denotes sum of the off-diagonal in a row. ···
80
81  T = 1500.00 K, p = 3.000E+03
82  From/To                          R             Pb
83  R                      9.48752E+06    9.48752E+06
84  Pb                     1.60158E+06    1.60158E+06
```

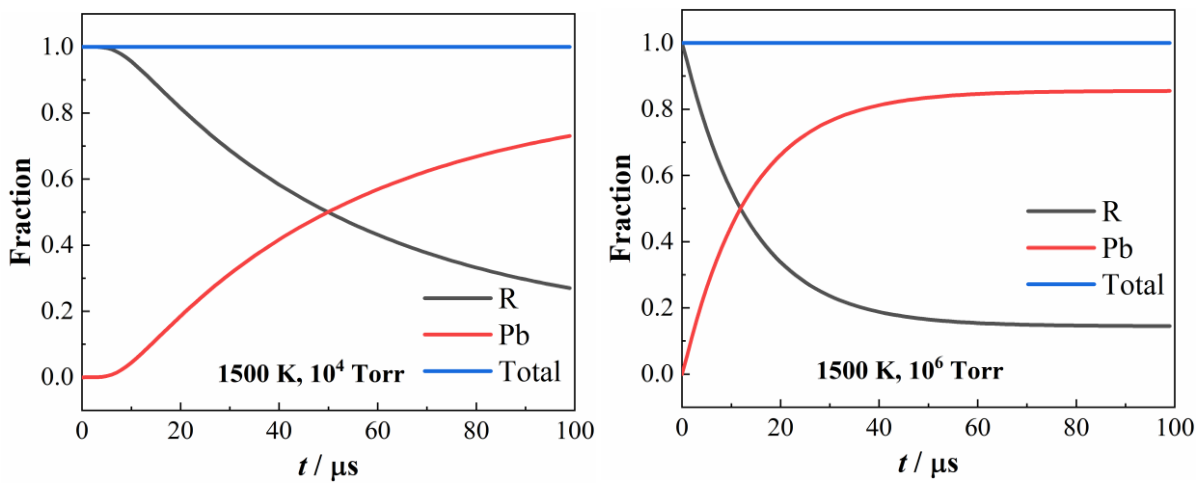
Phenomenological rate constants

```
204 ********************* Rate constants in temperature *********************
205
206 R -> other species
207  T[K]/p[torr]              3.000E+01      7.000E+01      1.000E+02      3.000E+02
208 1.500E+03                          #              #              #              #
209

224 ********************* High-pressure limit flux coefficient *********************
225
226 T[K]                          R->Pb          Pb->R
227 1.500E+03               6.92012E+07    1.16818E+07
228
```

```
128 ********************* Rate constants in pressure *********************
129
130 R -> other species
131  p[torr]/T[K]              1500.00
132 3.000E+01                       #
133 7.000E+01                       #
134 1.000E+02                       #
135 3.000E+02                       #
136 7.000E+02                       #
137 1.000E+03                       #
138 3.000E+03             9.48752E+06
139 7.000E+03             1.51666E+07
140 1.000E+04             1.81750E+07
141 3.000E+04             2.95969E+07
```

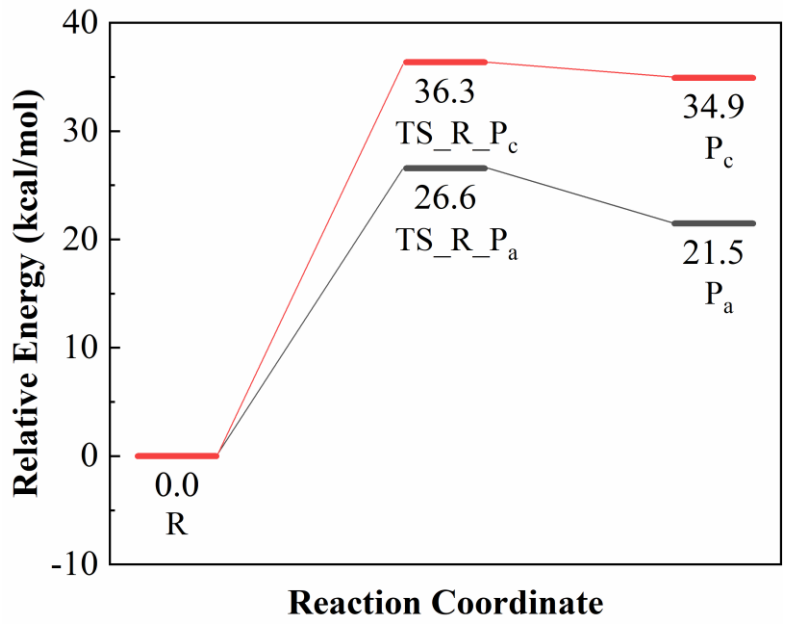
"Merge" happened

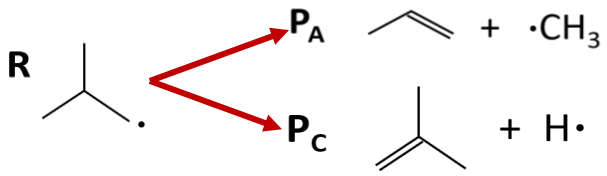


The time-evolution of isomers

Example 2

C-C and C-H *β*-scission of isobutyl





This is an example of competing unimolecular reactions. In this example, TST(RRKM) is used with the single-structure-rigid-rotor-harmonic-oscillator approximation. Rate constants are extracted from the master equation

$$\frac{d\mathbf{y}}{dt} = -\mathbf{W}\mathbf{y} + \mathbf{B}\mathbf{s} \qquad (2)$$

based on CSE theory, where $\mathbf{y}$ is a vector containing the population of R. For the time evolution, TUMME neglect the **Bs** term of eq (2) and uses the following homogeneous master equation:

$$\frac{d\mathbf{y}}{dt} = -\mathbf{W}\mathbf{y} \qquad (3)$$

Input: the standard input file
Output: rate constants and the time-evolution of concentrations.

Zhang, R. M.; Xu, X.; Truhlar, D. G., *The Journal of Physical Chemistry A* **2021,** *125* (28), 6303-6313.

Example 2 (cont.)

Standard input file

```
#nproc  15
#parallel mp

Parameter
    HSCollision
        Bmax[A]                 9.0
        MassM[amu]              28.0134
    End_HSCollision

    Edown
        EdConst[cm-1]           111.0324
    End_Edown

    Temperature[K]
        700.
    End_Temperature

    Pressure[torr]
     1E-10 1E-9 1E-8 1E-7 1E-6 1E-5 1E-4 1E-3 1E-2 1E-1 1.0 1E1 1E2 1E4 1E6
    End_Pressure

    GroundSpecies           R

    Precision quadruple
End_Parameter


Reaction
    BarrierRxn
        Info  R-TS_R_Pa-Pa
    End_BarrierRxn

    BarrierRxn
        Info  R-TS_R_Pc-Pc
    End_BarrierRxn
End_Reaction
```

Parallelism block

Parameter block

Collision section

Relaxation section

Temperature

Pressure

Species where zero of energy is placed

Precision of the transition matrix

Reaction block

Define the reactant, transition state and product

Example 2 (cont.)

Standard input file

```
Species
    Well                                                    Species block
        Name R
        Geometry[A]
            C                  0.00000100    0.06835100   -0.36837900
            ...
        End_Geometry
        Frequency[cm-1]
            76.5658               150.8529               176.9492
            ...
        End_Frequency
        E0K[eV]    2.937894765
    End_Well                                                Wells / isomers


    TranState
        Name TS_R_Pc
        Geometry[A]
            C                 -0.00000900    0.10844500    0.01394900
            ...
        End_Geometry
        Frequency[cm-1]
            83.0861               115.2996
            ...
        End_Frequency
        E0K[eV]       4.514114916
    End_TranState

    TranState                                               Transition states
        Name TS_R_Pa
        Geometry[A]
            C                 -0.31875100   -0.23524300   -0.46905000
            ...
        End_Geometry
        Frequency[cm-1]
            73.3727               118.3417
            ...
        End_Frequency
        E0K[eV]    4.089317803
    End_TranState

    Bim                                                     Bimolecular pairs
        Name Pa
        Sp1Mol                                              The first molecular fragment species
            Name  Pa_1 #sp1
            Geometry[A]
                C                 0.00000000    0.00000000    0.00000000
                ...
            End_Geometry
            Frequency[cm-1]
                920.0904              1304.9899              1304.9899
                ...
            End_Frequency
            E0K[eV]   0.0
            EleLevel[a.u.]
                1 0
            End_EleLevel
            Rotsigma        6
        End_Sp1Mol

        Sp2Mol                                              The second molecular fragment species
            Name  Pa_2 #sp2
            Geometry[A]
                C                -1.26496100   -0.21881800    0.03958700
                ...
            End_Geometry
            Frequency[cm-1]
                80.0033               438.0612               576.8934
                ...
            End_Frequency
            E0K[kcal/mol]  0.0
            Rotsigma        1.0
        End_Sp2Mol
        E0K[eV]  3.868742222
    End_Bim

    Bim
        Name Pc
        Sp1Mol
            Name  Pc_1 #sp1
            Geometry[A]
                C              0.000000    0.000000    1.456933
                ...
            End_Geometry
            Frequency[cm-1]
                29.8139           87.0421        393.0655
                ...
            End_Frequency
            E0K[kcal/mol]  0.0
            Rotsigma        2.0
        End_Sp1Mol

        Sp2Atom                                             The atomic fragment species
            Name      13_r #sp2
            Symbol    H
            E0K[kcal/mol] 0.0
        End_Sp2Atom
        E0K[eV]   4.452257969
    End_Bim

End_Species
```

Example 2 (cont.)

Standard output file

```
43  ********************** Global Parameter **********************
44    Precision:                  quadruple
45    MergeThreshold:             2.00000E-01
46    GroundSpecies:              R
47    <DeltaE_d>[a.u.]  =  (T/Tc)^(exponent)[ slope*( E - E_gamma,0) + EdConst ]
48        Tc[a.u.]:               9.50045E-04
49        exponent:               0.00000E+00
50        slope:                  0.00000E+00
51        EdConst[a.u.]:          5.05901E-04
52    HSCollision
53        bmax[a.u.]:             1.70075E+01
54        massM[a.u.]:            5.10653E+04
55        massA[a.u.]:            None
56
57  ************************** Isomers **************************
58    [MOLECULE PROPERTIES]
59    Name:                       R
60    Read from:                  SPECIES block
61    Number of atoms:            13
62  ›   Geometry [a.u.]:          ···
76    Freuencies scaling factor:  1.00000E+00
77  ›   Frequencies (scaled) [cm-1]: ···
87    E(ele) [ a.u.]:             -0.10796549924632348
88    ZPVE  [ a.u.]:              0.10796549924632348
89    E(0K) [ a.u.]:              0.0
90    Eletronic level [a.u.]:
91          1.00000E+00      0.00000E+00
92    Islinear:                   False
93    IABC [a.u.]:                1.11655E+17
94    Symmetry number:            1.00000E+00
95    Optical-isomer number:      1.00000E+00
96    MSTor file:                 None
97  [END OF MOLECULE]
```

Global parameters

Isomer properties

Elementary reactions

```
306  ********************** Reaction Stack **********************
307  [ REACTION INFO ]
308    Reactant:                   R
309    TS:                         TS_R_Pa
310    Product:                    Pa
311    Polyrate file:              None
312    Variation:                  tst
313    Tunneling:                  None
314    Lower limit of MEP:         None
315    Upper limit of MEP:         None
316    The k(E) will be calculated from the analytical expression.
317  [ END OF INFO ]
318
319  [ REACTION INFO ]
320    Reactant:                   Pa
321    TS:                         TS_R_Pa
322    Product:                    R
323    Polyrate file:              None
324    Variation:                  tst
325    Tunneling:                  None
326    Lower limit of MEP:         None
327    Upper limit of MEP:         None
328    The k(E) will be calculated from the analytical expression.
329  [ END OF INFO ]
```

Parameters for each (*T*, *p*) condition.

```
371 ⌄ ==================  Cycle  ==================
372
373    Temperature[K]:             7.000E+02
374    Pressure[Torr]:             1.000E-10
375    Energy step[cm-1]:          4.86525E+01
376    Energy reference[cm-1]:     2.73088E+04
377
378 ⌄ [ RELAXATION INFO ]
379    Name:                       R
380    Size:                       560
381    bmax[a.u.]:                 17.007535
382    Z[1/s]:                     3.117643E-03
383    Truncated well E0[cm-1]:    112.075
384    True well E0:[cm-1]         0.000
385  [ END OF INFO ]
386
387 ⌄ [ ME INFO ]
388    Size                        560
389    Min CSE eigenvalue[1/s]:    7.19400E-07
390    Max CSE eigenvalue[1/s]:    7.19400E-07
391    Min IERE eigenvalue[1/s]:   1.45896E-05
392    Max IERE eigenvalue[1/s]:   3.15746E+10
393
394 ⌄  EPCS:
395      CSE No.                   1
396      R                         9.61931E-01
397
398 ⌄  Kappa:
399      Bim Name                  Pa            Pc
400      R                         7.40531E-02   1.21092E-07
401
402 ⌄  Binding:
403      R well corresponds to eigen mode 1
404
405  [ END OF INFO ]
```

Example 2 (cont.)

Rate constants output file

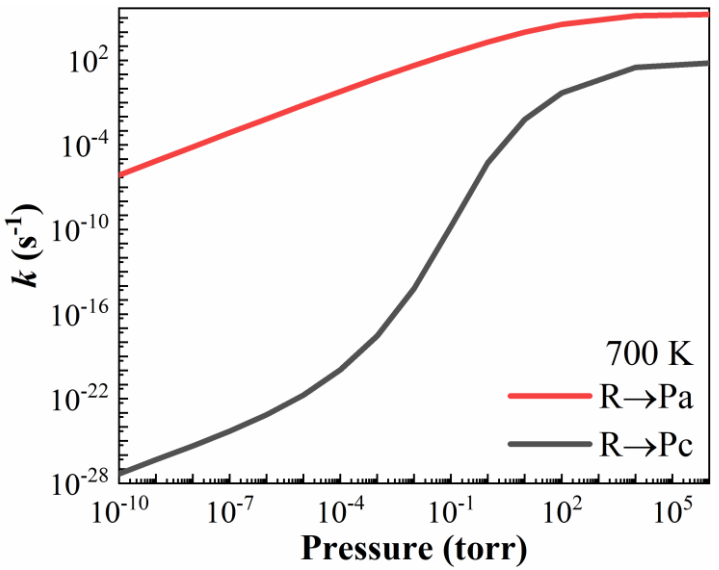
```
48  ********************* Rate constants map *********************
49  *   The diagonal denotes sum of the off-diagonal in a row.
50
51   T = 700.00 K, p = 1.000E-10
52   From/To                          R             Pa             Pc
53  R                       7.19400E-07    7.19400E-07    4.65869E-28
54  Pa                      2.58261E-26    2.53198E-18    2.53198E-18
55  Pc                      1.93973E-41    2.93664E-12    2.93664E-12
```

```
143  ******************** Rate constants in pressure ********************
144
145 R -> other species
146   p[torr]/T[K]               700.00
147  1.000E-10              7.19400E-07
148  1.000E-09              7.19367E-06
149  1.000E-08              7.19043E-05
150  1.000E-07              7.16146E-04
151  1.000E-06              7.01463E-03
152  1.000E-05              6.69286E-02
153  1.000E-04              6.14926E-01
154  1.000E-03              5.35435E+00
155  1.000E-02              4.32060E+01
156  1.000E-01              3.12770E+02
157  1.000E+00              1.94093E+03
158  1.000E+01              9.71923E+03
159  1.000E+02              3.61678E+04
160  1.000E+04              1.47466E+05
161  1.000E+06              1.76960E+05
```

Phenomenological rate constants

```
309  ******************** Rate constants in temperature ********************
310
311  R -> other species
312   T[K]/p[torr]             1.000E-10      1.000E-09      1.000E-08      1.000E-07
313  7.000E+02              7.19400E-07    7.19367E-06    7.19043E-05    7.16146E-04
```

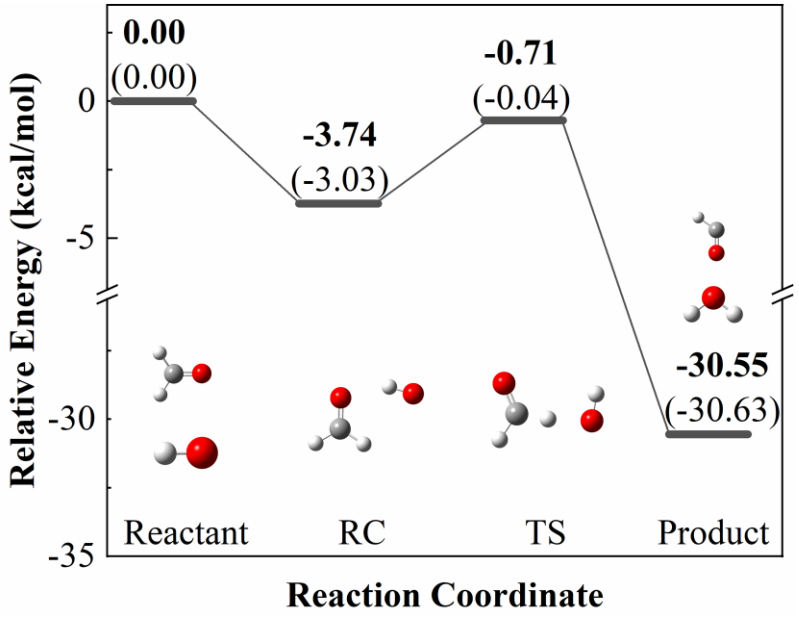
```
349  ******************** High-pressure limit flux coefficient ********************
350
351  T[K]                          R->Pa          R->Pc          Pa->R          Pc->R
352  7.000E+02              1.77507E+05    6.53738E+01    6.88689E-15    2.94171E-12
```



Falloff curves

Example 3

Hydrogen Abstraction from HCHO by OH (TST)



$$HCHO + OH \xrightarrow{1} HCHO\cdots HO \xrightarrow{2} HCO + H_2O$$

This is an example of a bimolecular reaction. This example uses TST(RRKM) theory with the single-structure-rigid-rotor-harmonic-oscillator is used for reaction 2, and the reaction 1 is estimated by the inverse-Laplacian transform to the hard-sphere model. Based on the CSE theory, the rate constant is extracted from

$$\frac{\mathrm{d}\mathbf{y}}{\mathrm{dt}} = -\mathbf{W}\mathbf{y} + \mathbf{B}n_{\mathrm{HCHO}}n_{\mathrm{OH}} \qquad (4)$$

where the $n_{\mathrm{HCHO}}n_{\mathrm{OH}}$ is left unknown. For time-evolution calculations, the reaction is assumed to be pseudo-first order, and eq. (4) is converted to homogeneous form by appending the n_{HCHO} concentration to the population vector $\mathbf{y}$ to get vector $\mathbf{y}^*$,

$$\frac{\mathrm{d}\mathbf{y}^*}{\mathrm{dt}} = -\mathbf{W}^*\mathbf{y}^* \qquad (5)$$

Input: the standard input file, *Polyrate* file for the reaction 2.
Output: rate constants and the time-evolution of concentrations.

Zhang, R. M.; Chen, W.; Truhlar, D. G.; Xu, X., *Faraday Discussions* **2022**, **238**, 431-460. doi.org/10.1039/D2FD00024E.

Example 3 (cont.)

Standard input file

```
Parameter
    LJCollision
        EpsilonM[cm-1]          56.993
        EpsilonA[cm-1]          191.134
        DiameterM[A]               3.74
        DiameterA[A]               4.94
        MassM[amu]              28
        MassA[amu]              47
    End_LJCollision

    Edown
        EDCONST[cm-1]    200
        Tc[K]            300
        Exponent         0.85
    END_Edown

    Temperature[K]
        600. 1000. 1500.
    End_Temperature

    Pressure[torr]
       1E-2
    End_Pressure

    PBimol
        BimolName
           R
        End_BimolName

        ExcessConc[mol/L]
           1E-5
        End_ExcessConc
    End_PBimol

    GroundSpecies           R
End_Parameter

Reaction
    BarrierRxn
        Info        RC-TS-P
        Pyrfile     Rxn1.fu6
    End_BarrierRxn

    BarrierlessRxn
        Info                    R-RC
        Avgdiameter[A]          4.11
        Rxnenergy[kcal/mol]   -3.734532
    End_BarrierlessRxn
End_Reaction
```

Global parameters block

Collision

Relaxation

Bimolecular pair(s) with pseudo-first order assumption

Reactions block

Barriered elementary reaction, read from Polyrate file

Barrierless elementary reaction , ILT + hard-sphere

```
Species
    Bim
        Name R
        Sp1Mol
            Name R_f
            Geometry[A]
                C      0.00000E+00      0.00000E+00     -5.23675E-01
                ......
            End_Geometry

            Frequency[cm-1]
                1.17074E+03 1.22857E+03 1.48038E+03 1.82298E+03 2.83467E+03 2.90356E+03
            End_Frequency
            EleLevel
            1 0
            End_EleLevel
            Rotsigma       2
            E0K[kcal/mol]  0
        End_Sp1Mol

        Sp2Mol
            Name R_h
            Geometry[A]
                O      0.00000E+00      0.00000E+00      1.07801E-01
                H      0.00000E+00      0.00000E+00     -8.62409E-01
            End_Geometry

            Frequency[cm-1]
                3.69902E+03
            End_Frequency

            EleLevel
              2 0
              2 0.000637887
            End_EleLevel

            E0K[kcal/mol] 0
        End_Sp2Mol
        E0K 0
    End_Bim

    Bim
        Name P
        Sp1Mol
            Name P_f
        End_Sp1Mol

        Sp2Mol
            Name P_w
            Rotsigma  2
        End_Sp2Mol
    End_Bim
End_Species
```

Species block

Example 3 (cont.)

Time-evolution file

```
#
# Time evolution ouput for TUMME
# the unit for energy is kcal/mol; the unit for time is second
#

T =           100.00   K, p =  1.000E+01 torr
y(E)/time                0.00000E+00    2.00000E-07    4.00000E-07    6.00000E-07
RC
7.94883E+00               6.85012E-32    8.33291E-22    7.96635E-22    7.61593E-22
7.90908E+00              -1.07883E-27    9.98076E-22    9.54173E-22    9.12200E-22
7.86934E+00              -3.32792E-28    1.19544E-21    1.14285E-21    1.09258E-21
7.82959E+00              -2.60212E-28    1.43168E-21    1.36871E-21    1.30850E-21
7.78985E+00               3.93483E-26    1.71456E-21    1.63914E-21    1.56703E-21
7.75011E+00              -4.70048E-27    2.05319E-21    1.96287E-21    1.87653E-21
7.71036E+00              -4.78735E-27    2.45852E-21    2.35037E-21    2.24698E-21
7.67062E+00              -3.84387E-27    2.94387E-21    2.81437E-21    2.69057E-21
7.63087E+00              -5.38489E-29    3.52505E-21    3.36998E-21    3.22174E-21
7.59113E+00               2.27151E-27    4.22076E-21    4.03509E-21    3.85760E-21
7.55139E+00              -1.03427E-26    5.05372E-21    4.83142E-21    4.61889E-21
7.51164E+00              -4.83806E-27    6.05073E-21    5.78457E-21    5.53012E-21
7.47190E+00              -1.73190E-26    7.24373E-21    6.92509E-21    6.62047E-21
7.43215E+00              -2.21353E-26    8.67143E-21    8.28999E-21    7.92533E-21
7.39241E+00              -5.47684E-27    1.03799E-20    9.92332E-21    9.48681E-21
7.35267E+00              -2.23638E-26    1.24241E-20    1.18776E-20    1.13551E-20
7.31292E+00              -2.15904E-26    1.48711E-20    1.42169E-20    1.35915E-20
7.27318E+00              -1.11184E-26    1.77991E-20    1.70162E-20    1.62676E-20
7.23343E+00              -2.36191E-26    2.13020E-20    2.03649E-20    1.94691E-20
7.19369E+00              -1.19291E-26    2.54929E-20    2.43715E-20    2.32994E-20
```

time

energy

microscopic population of RC

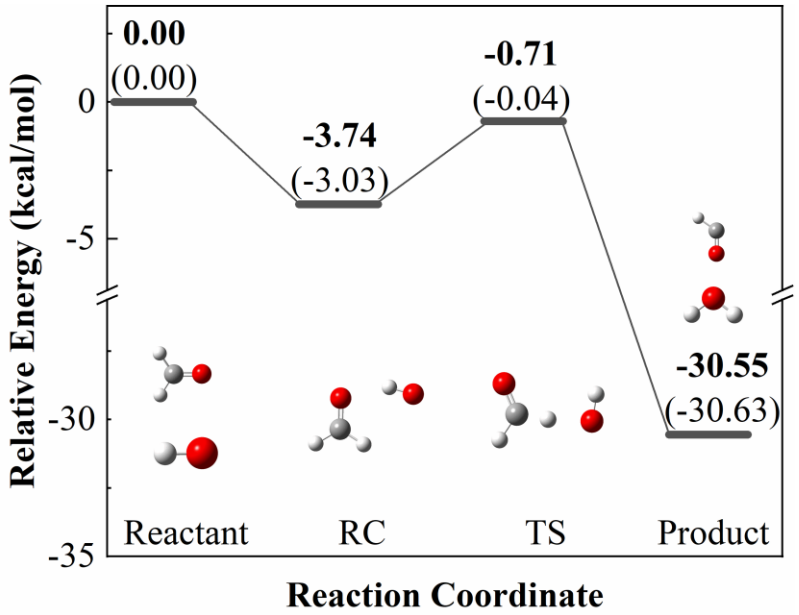
```
R
[n]                      1.00000E+00    9.56011E-01    9.13957E-01    8.73754E-01    8.35318E-01
```

macroscopic concentration of R

The time-evolution of n_{OH} (solid lines) and n_{RC} (dash-dot lines). The initial condition is set as $n_{OH}(t)=0=10^{-7}$ mol/L, $n_{RC}(t)=0$ and n_{HCHO} is assumed to be constant at 10^{-5} mol/L.

Example 4

Hydrogen Abstraction from HCHO by OH (MS-VTST/SCT)



This is an example of a bimolecular reaction. In this example, MS-CVT/SCT is used for reaction 2, and rate constants for reaction 1 are estimated by an inverse Laplace transform applied to the hard-sphere model. The rate constant is extracted from eq. (4) based on CSE theory, and the time evolution is estimated from eq. (5).

Input: the standard input file,
Polyrate file for reaction 2,
MStor files for RC and TS
Output: rate constants and the time-evolution of concentrations.

$$HCHO + OH \xrightarrow{1} HCHO\cdots HO \xrightarrow{2} HCO + H_2O$$

Zhang, R. M.; Chen, W.; Truhlar, D. G.; Xu, X., *Faraday Discussions* **2022**, **238**, 431-460. doi.org/10.1039/D2FD00024E.

Example 4 (cont.)

Standard input file

```
Parameter
    LJCollision
        EpsilonM[cm-1]          56.993
        EpsilonA[cm-1]          191.134
        DiameterM[A]               3.74
        DiameterA[A]               4.94
        MassM[amu]              28
        MassA[amu]              47
    End_LJCollision

    Edown
        EDCONST[cm-1]    200
        Tc[K]            300
        Exponent         0.85
    END_Edown

    Temperature[K]
        100.
      End_Temperature

    Pressure[torr]
       10 1E4 1E7
    End_Pressure

    PseuBimolecular
        PseuBimName
           R
        End_PseuBimName

        ExcessConc[mol/L]
           1E-5
        End_ExcessConc
    End_PseuBimolecular

    GroundSpecies           R
End_Parameter
```

Global parameters block

Collision

Relaxation

Bimolecular pair(s) with pseudo-first order assumption

```
Reaction

    BarrierRxn
        Info          RC-TS-P
        Pyrfile      Rxn1.fu6
        Variation     cvt
        Tunneling     sct
        slower[A]     -0.12
        supper[A]      0.23
    End_BarrierRxn

    BarrierlessRxn
        Info                    R-RC
        Avgdiameter[A]          4.11
        Rxnenergy[kcal/mol]   -3.734532
    End_BarrierlessRxn

End_Reaction

Species
    Bim
        Name R
        Sp1Mol
            Name R_f
            Geometry[A]
                .
                .
                .
```

Reactions block

Barriered elementary reaction, read from Polyrate file

Variation

Tunneling

Range of reaction coordinates

Barrierless elementary reaction , ILT + hard-sphere

Species block

Example 4 (cont.)

- Time-evolution file

```
#
# Time evolution ouput for TUMME
# the unit for energy is kcal/mol; the unit for time is second
#

T =          100.00   K, p =  1.000E-03 torr
y(E)/time              0.00000E+00    2.00000E-07    4.00000E-07    6.00000E-07    8.00000E-07
RC
9.93603E+00           -7.69770E-42    4.93115E-26    4.77741E-26    4.62847E-26    4.48416E-26
9.91602E+00            0.00000E+00    5.40583E-26    5.23729E-26    5.07401E-26    4.91581E-26
9.89601E+00            2.30931E-41    5.92603E-26    5.74127E-26    5.56227E-26    5.38885E-26
9.87599E+00           -6.15816E-41    6.49632E-26    6.29379E-26    6.09756E-26    5.90746E-26
9.85598E+00            1.53954E-41    7.12143E-26    6.89940E-26    6.68430E-26    6.47590E-26
9.83596E+00            0.00000E+00    7.80675E-26    7.56336E-26    7.32755E-26    7.09910E-26
9.81595E+00            7.69770E-41    8.55779E-26    8.29098E-26    8.03249E-26    7.78206E-26
9.79594E+00           -1.53954E-41    9.38099E-26    9.08852E-26    8.80516E-26    8.53064E-26
9.77592E+00            1.53954E-41    1.02833E-25    9.96269E-26    9.65208E-26    9.35115E-26
9.75591E+00           -3.07908E-41    1.12723E-25    1.09209E-25    1.05804E-25    1.02505E-25
9.73589E+00            9.23724E-41    1.23566E-25    1.19713E-25    1.15981E-25    1.12365E-25
9.71588E+00           -1.53954E-40    1.35448E-25    1.31225E-25    1.27134E-25    1.23170E-25
9.69587E+00            9.23724E-41    1.48469E-25    1.43840E-25    1.39355E-25    1.35010E-25
9.67585E+00            3.07908E-41    1.62743E-25    1.57669E-25    1.52754E-25    1.47991E-25
9.65584E+00           -6.15816E-41    1.78390E-25    1.72828E-25    1.67440E-25    1.62219E-25
9.63582E+00            1.84745E-40    1.95535E-25    1.89439E-25    1.83533E-25    1.77811E-25
9.61581E+00           -1.53954E-40    2.14328E-25    2.07646E-25    2.01172E-25    1.94900E-25
```

time

energy

microscopic population of RC

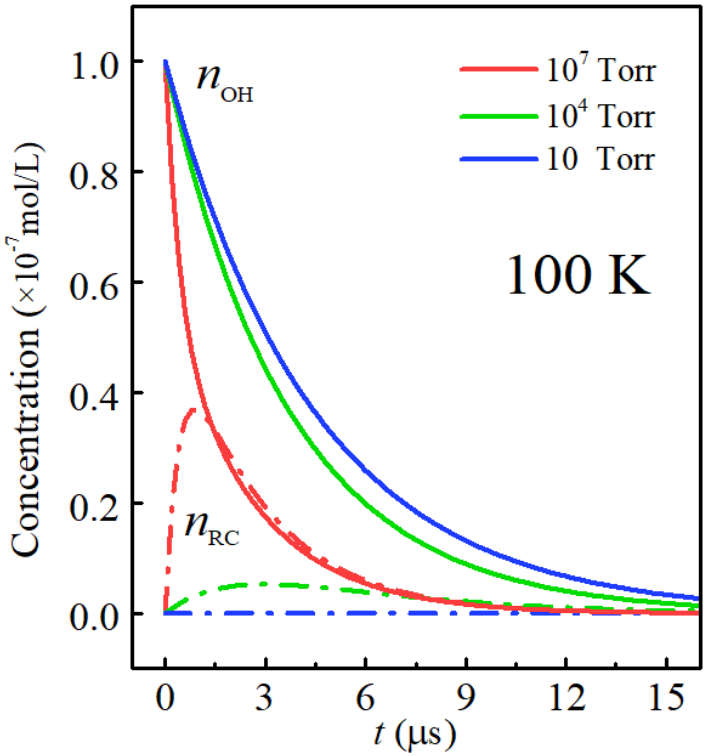
```
R
[n]                    1.00000E+00    9.68821E-01    9.38616E-01    9.09352E-01    8.81001E-01
```

macroscopic concentration of R

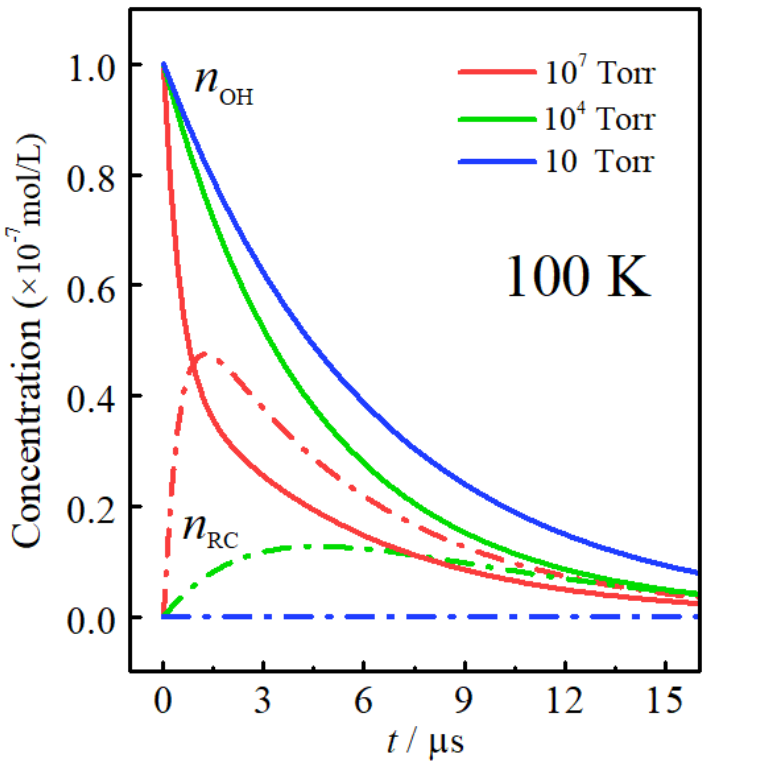
The time evolution of n_{OH} (solid lines) and n_{RC} (dash-dot lines). The initial condition is set as $n_{OH}(t=0)=10^{-7}$ mol/L; $n_{RC}(t=0)$ and n_{HCHO} are assumed to be constant at 10^{-5} mol/L.

Example 4 (cont.)

- Comparison with example 3



Time-evolution of the example 3 (TST)



Time-evolution of the example 4 (VTST)

Thank you for your interest in TUMME.

You are invited to provide feedback to: xuxuefei@tsinghua.edu.cn and truhlar@umn.edu

The authors gratefully acknowledge Wenqi Chen for assistance with the tutorial.