

SUPPORTING INFORMATION  
FOR AN ARTICLE IN *FARADAY DISCUSSIONS*  
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**Master Equation Study of Hydrogen Abstraction from HCHO by OH Via a Chemically Activated Intermediate**

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# 1. Cartesian coordinates (Å) of reactants, reactive complex, transition state, and products

Geometries are optimized under M08-HX/aug-cc-pVTZ level.

## HCHO

C	0.000000000	0.000000000	-0.523675000
O	0.000000000	0.000000000	0.669924000
H	0.000000000	0.942526000	-1.108670000
H	0.000000000	-0.942526000	-1.108670000

## OH

O	0.000000000	0.000000000	0.107801000
H	0.000000000	0.000000000	-0.862409000

## HCHO...HO

C	1.132277000	0.654751000	0.000000000
H	1.985084000	1.359437000	0.000000000
H	1.364435000	-0.427808000	0.000000000
O	0.000000000	1.048580000	0.000000000
O	-1.135727000	-1.580307000	0.000000000
H	-1.057360000	-0.606321000	0.000000000

## TS

C	-0.858500126	-0.209729348	0.000000000
H	-1.874245272	0.242127167	0.000000000
H	0.001566889	0.549333610	0.000000000
O	-0.673150503	-1.380443522	0.000000000
O	1.312460121	1.443103400	0.000000000
H	1.948361838	0.711293599	0.000000000

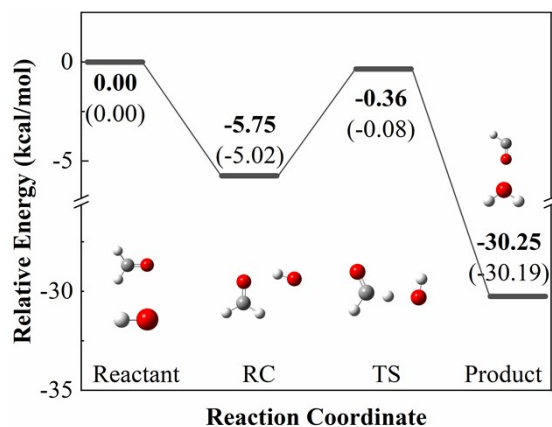
## HCO

C	0.061969000	0.579126000	0.000000000
H	-0.867563000	1.214839000	0.000000000
O	0.061969000	-0.586199000	0.000000000

## H<sub>2</sub>O

O	0.000000000	0.000000000	0.115478000
H	0.000000000	0.762497000	-0.461914000
H	0.000000000	-0.762497000	-0.461914000

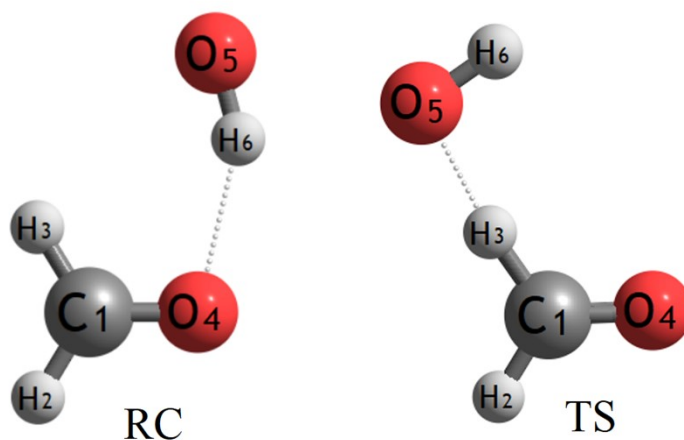
## 2. Electronic energy profile



**Figure S1.** M08-HX/aug-cc-pVTZ potential energy profile (excluding ZPE) for formaldehyde reaction with hydroxyl. Values in parenthesis are benchmarks obtained by CCSD(T)-F12b/jul-cc-pVTZ//CCSD(T)/aug-cc-pVTZ. The CCSD(T)/aug-cc-pVTZ geometries are from M. A. Ali and J. R. Barker, *J. Phys. Chem. A*, **2015**, 119, 7578–7592.

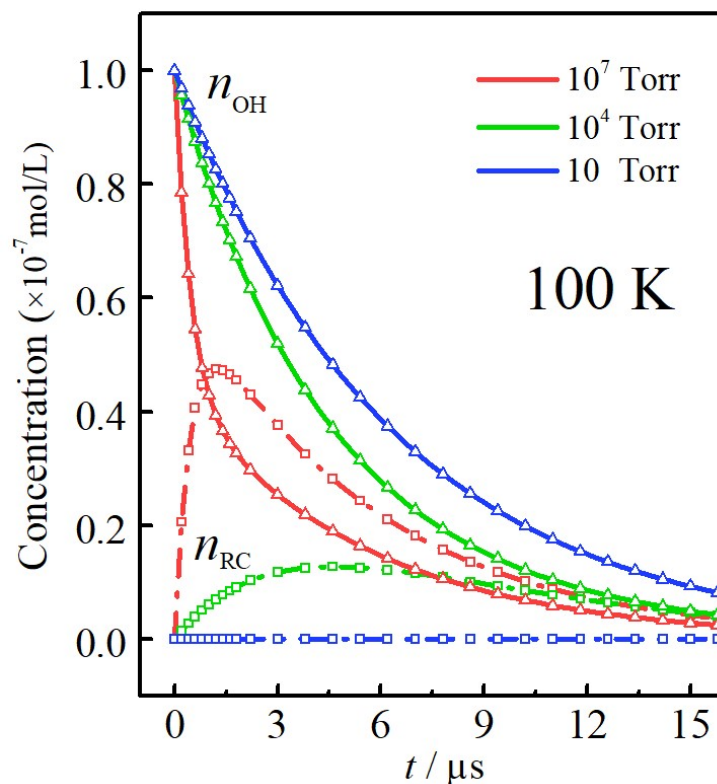
### 3. Torsional anharmonicity

The torsional anharmonicity of each species is calculated by the MS-T method. As shown in Fig. S2, the torsional dihedral for RC is defined as O5-O4-C1-H2, and the torsional dithedals for TS are defined as H2-C1-O4-O5 and H6-O5-C1-O4. Note that MS-T provides a useful treatment of the torsional anharmonicity even cases like the present one, where each species has only one conformation.



**Figure S2.** Geometries of reaction complex and transition structure.

#### 4. Verification of rate constants



**Figure S3.** Concentrations of OH and RC as functions of time.

Concentrations obtained by using all the eigenmodes of the pseudo-first-order homogenous master equation by the method of Section 2.2. [eqn (11)] are shown by lines. The solid lines are for OH radical, and the dash-dot lines are for RC. The initial conditions for the results obtained by this method are

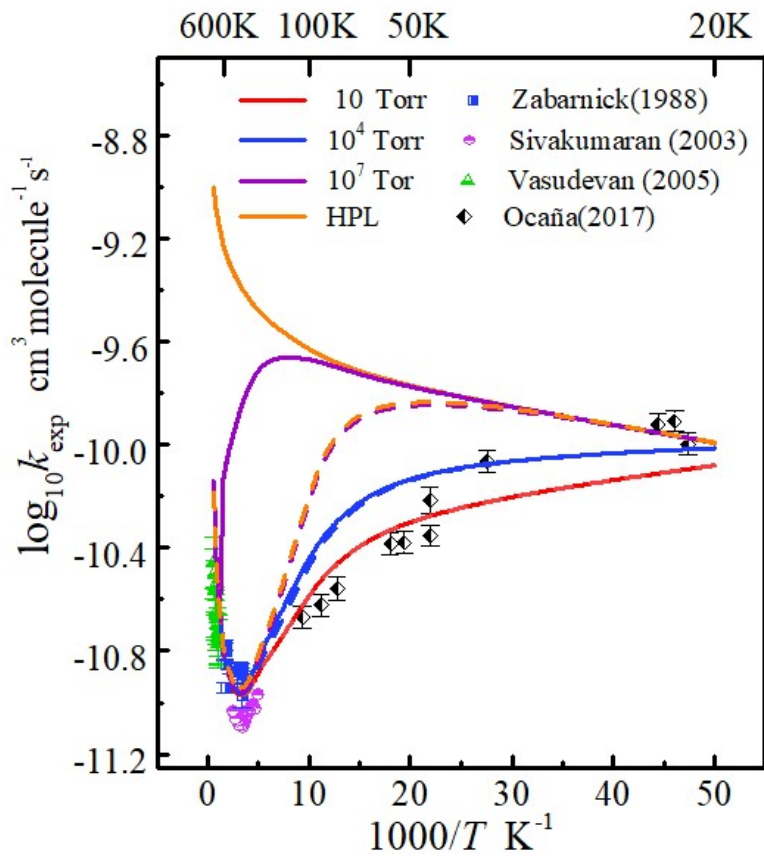
$$n_{OH}(t = 0) = 10^{-7} \text{ mol/L}$$

$$n_{RC}(t = 0) = 0$$

$$n_{HCHO} = 10^{-5} \text{ mol/L}$$

Concentrations are also calculated from eqns (30) and (31) by using the phenomenological rate constants obtained from the CSE eigenmode of the nonhomogeneous master equation by the method of Section 2.4; these concentrations are indicated by symbols. Even though this rate constant calculation does not involve the pseudo-first-order assumption, the time evolutions produced by the rate constants match perfectly well with those calculated from eqn (11).

## 5. Experimentally observed rate constants



**Figure S4.** Like Figures 8 and 9 but plotted as a single Arrhenius plot to show the overall trends better.

## 6. The seven lowest eigenvalues of the G matrix at various pressures

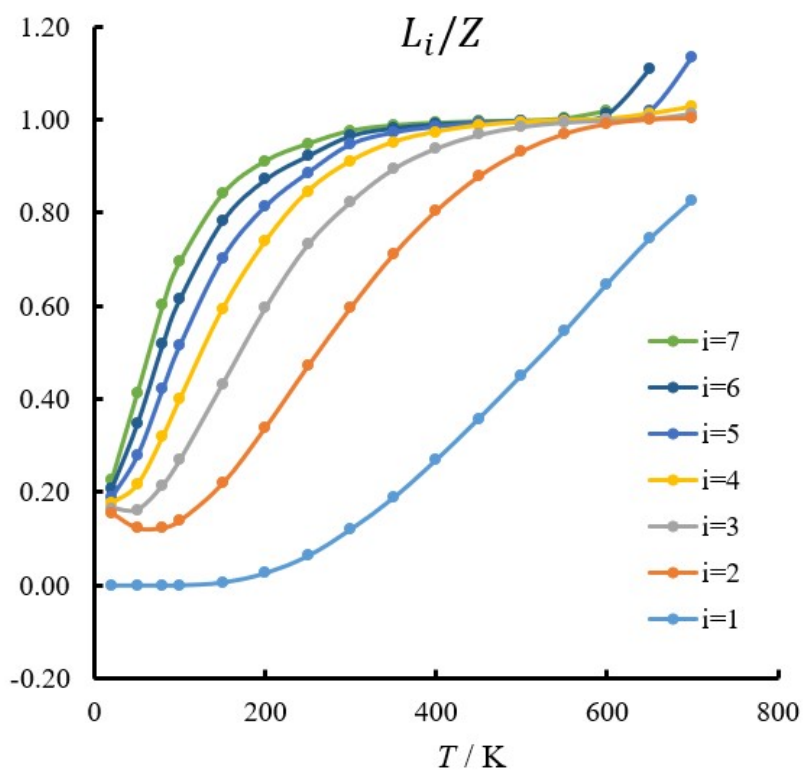


Figure S5. Seven lowest eigenvalues of  $\mathbf{G}$  at  $10^{-2}$  Torr

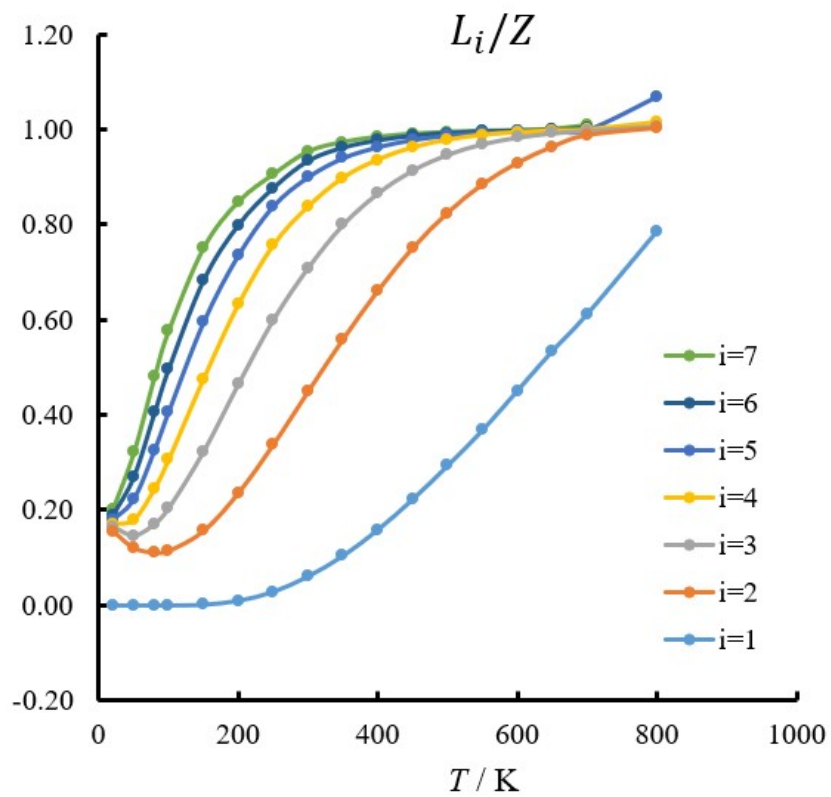


Figure S6. Seven lowest eigenvalues of  $\mathbf{G}$  at 10 Torr.



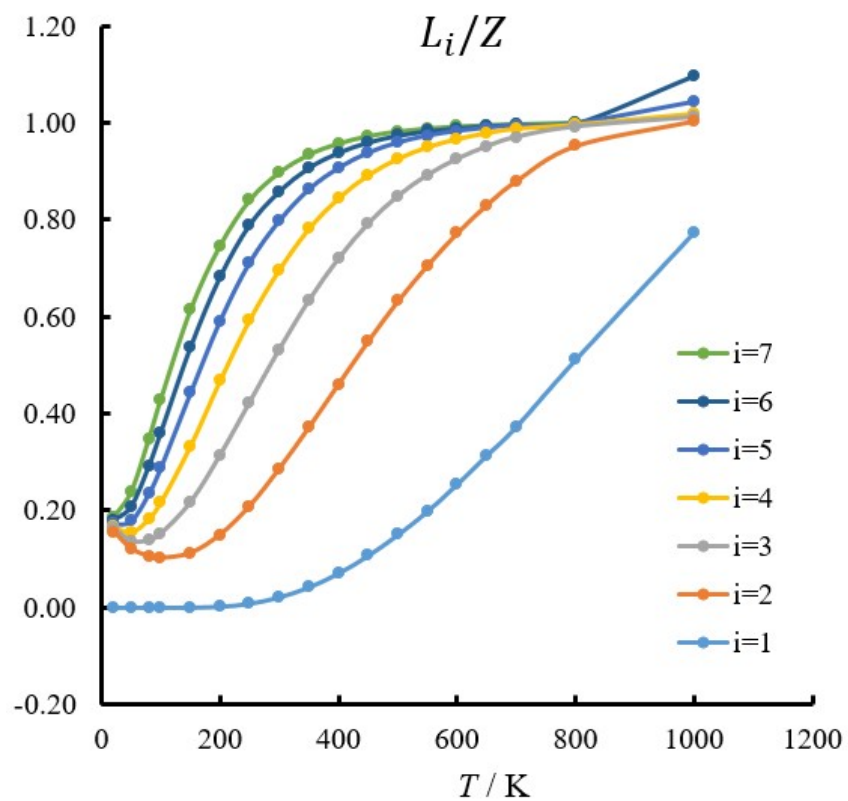
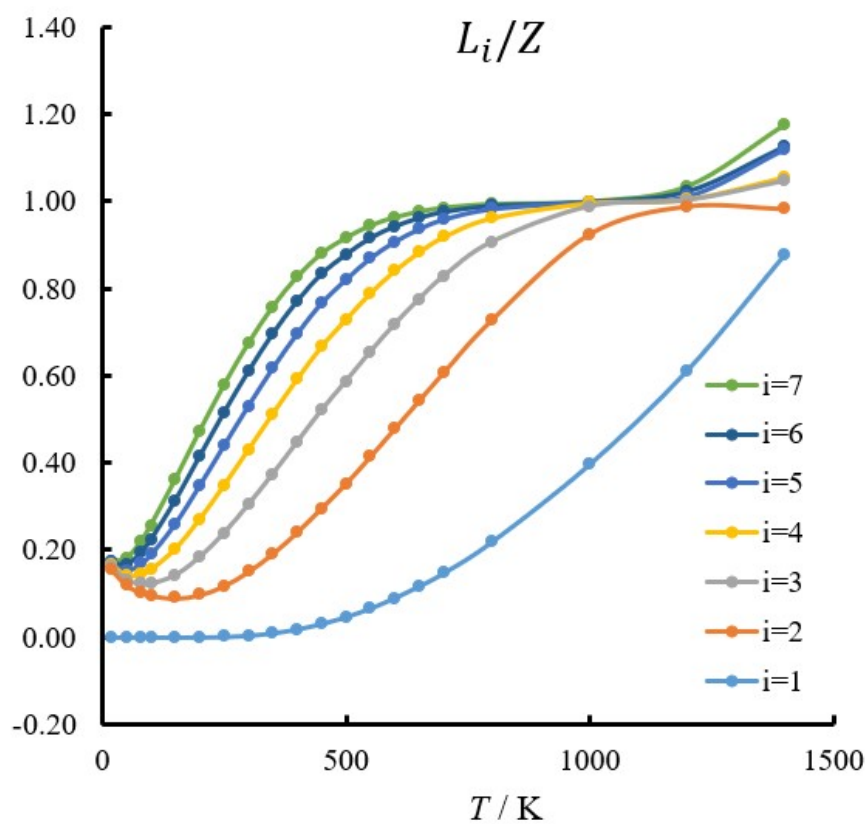


Figure S7. Seven lowest eigenvalues of  $G$  at  $10^4$  Torr.



**Figure S8.** Seven lowest eigenvalues of  $\mathbf{G}$  at  $10^7$ Torr.

## 7. Verification of the detailed balance condition

Rate constants should satisfy the macroscopic detailed balance condition. Georgievskii et al. have concluded [Y. Georgievskii, J. A. Miller, M. P. Burke and S. J. Klippenstein, *J. Phys. Chem. A*, 2013, **117**, 12146–12154.] that – as long as the CSE assumption is good – the phenomenological rate constants

extracted from master equations satisfy this requirement. Therefore  $k_{RC \rightarrow R}$  and  $k_{R \rightarrow RC}$  are not independent, and their ratio should equal the equilibrium constant. Table S1 shows that when the assumptions of CSE theory are satisfied very well, the ratio of forward to backward rate constant equals the equilibrium constant to a good approximation. In the table, HPL denotes the high-pressure limit, which is the equilibrium constant. Table S2 shows that when the assumptions of CSE theory are not well satisfied, the ratio of forward to backward rate constant deviates from the equilibrium constant

**Table S1** Ratio of  $k_{R \rightarrow RC}/k_{RC \rightarrow R}$

T/K	p/Torr	10 <sup>-2</sup>	10	10 <sup>4</sup>	10 <sup>7</sup>	HPL <sup>a</sup>
20		5.41E+18	5.41E+18	5.41E+18	5.41E+18	5.41E+18
50		1.86E-07	1.86E-07	1.86E-07	1.86E-07	1.86E-07
80		4.90E-14	4.90E-14	4.90E-14	4.90E-14	4.90E-14
100		2.85E-16	2.85E-16	2.85E-16	2.85E-16	2.85E-16
150		2.66E-19	2.75E-19	2.77E-19	2.78E-19	2.78E-19
200		7.09E-21 <sup>a</sup>	7.89E-21	8.36E-21	8.48E-21	8.48E-21
250			8.85E-22	1.02E-21	1.08E-21	1.09E-21
300				2.39E-22	2.77E-22	2.84E-22
350					1.08E-22	1.15E-22
400					5.25E-23	5.98E-23
450					2.98E-23	3.71E-23

**Table S2** Ratio of  $k_{R \rightarrow RC}/k_{RC \rightarrow R}$

T/K	p/Torr	10 <sup>-2</sup>	10	10 <sup>4</sup>	10 <sup>7</sup>	HPL <sup>c</sup>
200		7.09E-21 <sup>a</sup>	7.89E-21	8.36E-21	8.48E-21	8.48E-21
250		7.27E-22	8.85E-22	1.02E-21	1.08E-21	1.09E-21
300		1.40E-22 <sup>b</sup>	1.87E-22	2.39E-22	2.77E-22	2.84E-22
350			5.91E-23	8.29E-23	1.08E-22	1.15E-22
400				3.55E-23	5.25E-23	5.98E-23
450				1.76E-23	2.98E-23	3.71E-23
500					1.87E-23	2.59E-23
550					1.26E-23	1.97E-23
600					8.88E-24	1.59E-23
650					6.51E-24	1.35E-23
700					4.93E-24	1.19E-23

a: Cells highlighted in blue correspond to a merger threshold of  $P = 0.2$ .

b: Cells highlighted in yellow correspond to a merger threshold of  $P = 0.6$ .

## 8. Input for *TUMME 3.0*

This file is the input file for *TUMME 3.0* to calculate CSE rate constants, pseudo-first-order time evolution, and eigenvalues of **G**.

```
#parallel mpi
#nproc 22
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]
    20. 50. 80. 100. 150. 200. 250. 300. 350. 400. 450. 500.
    550 600. 650. 700. 800. 1000. 1200. 1400. 1600. 1800.
  End_Temperature

  Pressure[torr]
    1E-2 1E1 1E4 1E7
  End_Pressure

  PseuBimolecular
    PseuBimName
      R
    End_PseuBimName

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

  Energy
    ESOT 0.1
    EEOT 50
    dE[cm-1] 0.2
    Emax[kcal/mol] 400
  End_Energy

  Print
    Eigenvalue
      evalfile eval.out
      evalnum 7
    End_Eigenvalue

    TimeEvolution
      TimeFile time.txt
      TimeNum 200
      TimeStep[s] 2E-7
```

```
InitSpecies
  R
End_InitSpecies
End_TimeEvolution
End_Print

GroundSpecies      R
MergeThreshold     0.2
Precision          quadruple
End_Parameter

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]
  C      0.00000E+00      0.00000E+00      -5.23675E-01
  O      0.00000E+00      0.00000E+00      6.69924E-01
  H      0.00000E+00      9.42526E-01      -1.10867E+00
  H      0.00000E+00      -9.42526E-01     -1.10867E+00
  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
    EOK 0
End_Bim

Well
  Name      RC
  MSTfile   mstor_complex.out
End_Well

TranState
  Name      TS
  MSTfile   mstor_TS.out
End_TranState

Bim
  Name P
  Sp1Mol
    Name P_f
    End_Sp1Mol

    Sp2Mol
      Name P_w
      Rotsigma 2
      End_Sp2Mol
  End_Bim
End_Species
```

## 9. Input for *Polyrate 2017*

This file is the input file for *Polyrate 2017* to calculate CSE rate constants, pseudo-first-order time evolution, and eigenvalues of **G**.

\*General

```
TITLE
  HCOH-OH -> HCO + H2O
  Gausrate Test Calculation (M08HX/aug-cc-pVTZ Level)
END
```

```
ATOMS
  1    C
  2    H
  3    H
  4    O
  5    O
  6    H
END
```

NOSUPERMOL

```
RESTART
  writefu1
END
```

\*OPTIMIZATION

```
OPTMIN  OHOOK
OPTTS   OHOOK
```

\*SECOND

```
FPRINT
HESSCAL  HHOOK
```

\*REACT1

```
INITGEO  GEOM
```

STATUS 2

```
GEOM
1      1.132277000      0.654751000      0.000000000
2      1.985084000      1.359437000      0.000000000
3      1.364435000     -0.427808000      0.000000000
4      0.000000000      1.048580000      0.000000000
5     -1.135727000     -1.580307000      0.000000000
6     -1.057360000     -0.606321000      0.000000000
END
```

```
ELEC
  2    0.0
END
```

SPECIES NONLINRP

\*PROD1

```
INITGEO  GEOM
STATUS 2
GEOM
1      0.061969000      0.579126000      0.000000000
2     -0.867563000      1.214839000      0.000000000
4      0.061969000     -0.586199000      0.000000000
END
ELEC
  2  0.0
END
```

SPECIES NONLINRP

\*PROD2

```
INITGEO  GEOM
STATUS 2
GEOM
5      0.000000000      0.000000000      0.115478000
3      0.000000000      0.762497000     -0.461914000
6      0.000000000     -0.762497000     -0.461914000
END
ELEC
  1  0.0
END
```

SPECIES NONLINRP

\*START

```
INITGEO  GEOM
STATUS 2
GEOM
1     -0.858500126     -0.209729348      0.000000000
2     -1.874245272      0.242127167      0.000000000
3      0.001566889      0.549333610      0.000000000
4     -0.673150503     -1.380443522      0.000000000
5      1.312460121      1.443103400      0.000000000
6      1.948361838      0.711293599      0.000000000
END
ELEC
  2  0.0
END
```

SPECIES NONLINTS

\*PATH

```
SCALEMASS  1.000000
SSTEP      0.005
INH         9
NSTEPS     99999
CURV       dgrad
```



---

```
FIRSTSTEP      nmode
RPM            pagem
FREQSCALE     0.975
RODS          on
# in au
SSPECIAL
-2.50
-1.66
-1.00
-1.04
-0.2154288
-0.2040904
-0.1927521
-0.1814137
-0.1700753
-0.1587370
-0.1473986
-0.1360603
-0.1247219
-0.1133836
-0.1020452
-0.0907068
-0.0793685
-0.0680301
-0.0566918
-0.0453534
-0.0340151
-0.0226767
-0.0113384
0.0000000
0.0113384
0.0226767
0.0340151
0.0453534
0.0566918
0.0680301
0.0793685
0.0907068
0.1020452
0.1133836
0.1247219
0.1360603
0.1473986
0.1587370
0.1700753
0.1814137
0.1927521
0.2040904
0.2154288
0.2267671
0.2381055
0.2494438
0.2607822
0.2721205
0.2834589
0.2947973
0.3061356
0.3174740
0.3288123
0.3401507
0.3514890
0.3628274
0.3741657
0.3855041
```

```
0.3968425
0.4081808
0.4195192
0.4308575
0.4421959
0.4535342
0.4648726
0.4762110
0.4875493
0.4988877
0.5102260
0.5215644
0.5329027
0.5442411
END
```

```
SRANGE
  slp 1.0
  slm -3.0
END
```

```
COORD      curv3
```

```
INTDEF
2-1
3-1
4-1
5-3
6-5
5-1
5-3-1
2-1-5
2-1-3
4-1-3
4-1-2
4-1-5
6-5-3
2-3-4-1
5-1-4-2
5-3-1-4
1-3-5-6
END
```

```
PRINTSTEP
```

```
*TUNNEL
```

```
ZCT
SCT
```

```
QUAD
  NQE 40
  NQTH 40
  NSEGBOLTZ 1
  NSEGTHETA 1
END
```

```
SCTOPT
  LAGRANGE 6
END
```

```
*RATE
```

---

BOTHK  
SIGMAF 1  
SIGMAR 2  
TST  
CVT

PRDELG  
PRPART r

TEMP  
20.  
50.  
80.  
100.  
150.  
200.  
213.  
225.  
250.  
298.15  
300.  
350.  
400.  
450.  
500.  
550  
600.  
650.  
700.  
800.  
1000.  
1200.  
1400.  
1600.  
1800.

END