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Reanalysis of Rate Data for the Reaction $CH_3 + CH_3 \rightarrow C_2H_6$ Using Revised Cross-Sections and a Linearised Second Order Master Equation

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SUPPORTING INFORMATION I

1. Log file from PGOPHER[1] fit to the available ground state data.

The file is attached as Supporting Information III, as a text file. It also gives the constants for all the states used in Model I.

2. Correction factors for absorption cross sections

Table S1. Correction factors for rate coefficients based on the absorption cross sections derived in Section 2. The rate coefficients obtained by absorption spectroscopy, and tabulated in Table II of Slagle et al.,[2] were multiplied by the factors given below to correct for errors in the absorption cross sections used in the paper. The temperature dependent factors needed for a 0.6 nm bandpass are included (see Section 2)

T/K	Model I	Model II
296	1.00	1.00
407	1.02	1.01
474	1.05	1.02
513	1.09	1.05
539	1.11	1.06
577	1.14	1.08
700	1.13	1.01
810	1.08	0.922
906	0.970	0.793

3. The results of fitting the data used in Fit 5, but with different energy transfer parameters above and below 1000 K. χ^2/(degree of freedom) is essentially the same as in Table 3, fit 5.

Energy transfer parameters 300 – 1000 K

T_{ref} = 298 K; $\langle\Delta E\rangle_{down,ref}$ = 282 cm^{-1}, m = 0.65

Energy transfer parameters 1350 K – 2034 K.

T_{ref} = 1400 K; $\langle\Delta E\rangle_{down,ref}$ = 677 cm^{-1}, m = -0.09

Golden[11] fitted the data of Slagle et al.[2] and Oehlschlaeger et al.[4] using a stochastic master equation, with $k(E)$ calculated with a Gorin model, constrained to the $k_\infty(T)$ values of Klippenstein et al..[12] He obtained significantly lower values of $\langle\Delta E\rangle_{down}$ for Ar, increasing from 10 cm^{-1} at 296 K to 233 cm^{-1} at 1924 K. He also found that $\langle\Delta E\rangle_{down}$ increased more rapidly with T for T<1000 K than it did for T>1000K. The parameters shown above give $\langle\Delta E\rangle_{down}$ reaching a maximum of 677 cm^{-1} at 1400 K and then decreasing slightly with increasing temperature. The reason for the lower values for the energy transfer parameters from the fits by Golden, especially at low T is not clear but indicates smaller values for $k(E)$ using the Gorin model compared with those from the ILT fits used here. These differences could derive from the different treatments of the rotational degrees of freedom in the transition state (all implicitly active in the ILT method, only the K-rotor active in the Gorin model).

4. The results of extending the data used in Fit 5 to include the experimental data of Du et al.[3]

Figure S1 shows a plot of the experimental values vs the calculated values for Fit 5 and also includes the experimental data of Du et al.[3] The insert expands the low pressure region and shows that the data from Du et al. fall systematically below the best fit line and show more scatter than do the data of Oehlshlaeger et al.[4] χ^2/(degree of freedom) = 1.65

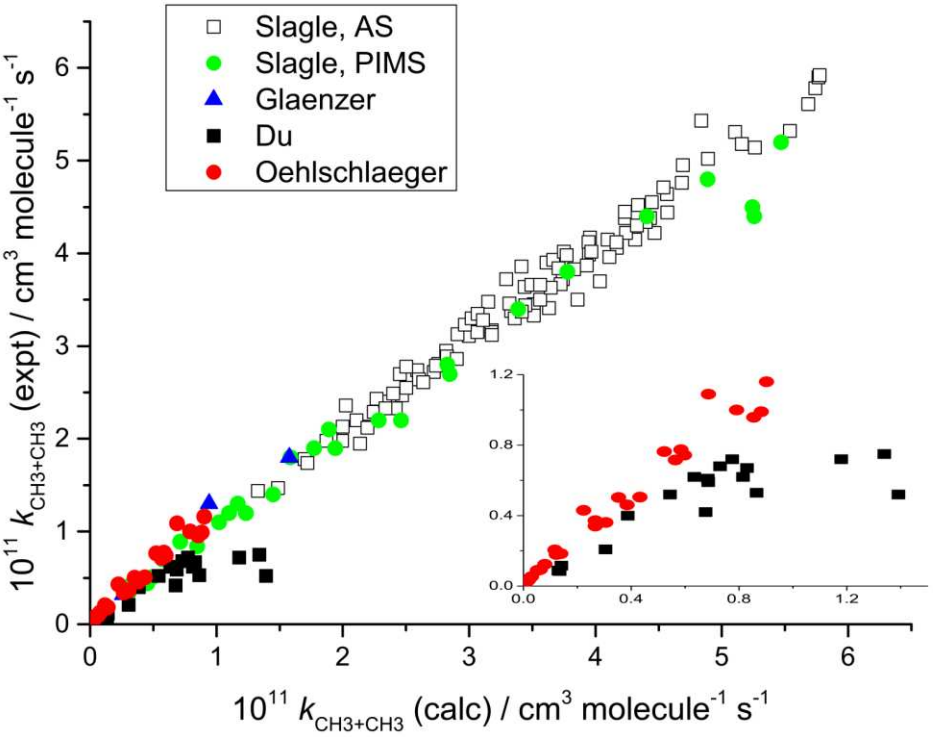

Figure S1. Plot of the experimental rate coefficients in Ar vs the best fit values from the master equation, including the high temperature data of Du et al.[3] The data refer to: Slagle et al.,[2] Glänzer et al.,[5] Du et al.,[3] Oehlschlaeger et al.[4]

5. The results of extending the data used in Fit 5 to include the experimental data of Yang et al.[6]

Figure S2 shows a plot of the experimental values vs the calculated values for Fit 5 and also includes the experimental data of Yang et al.[6] The latter were fitted using independent energy transfer parameters for Kr. The resulting parameters are:

T_{ref} = 1500 K; $\langle\Delta E\rangle_{down,ref}$ = 331 cm^{-1}, m = 0.40, χ^2/(degree of freedom) = 1.72

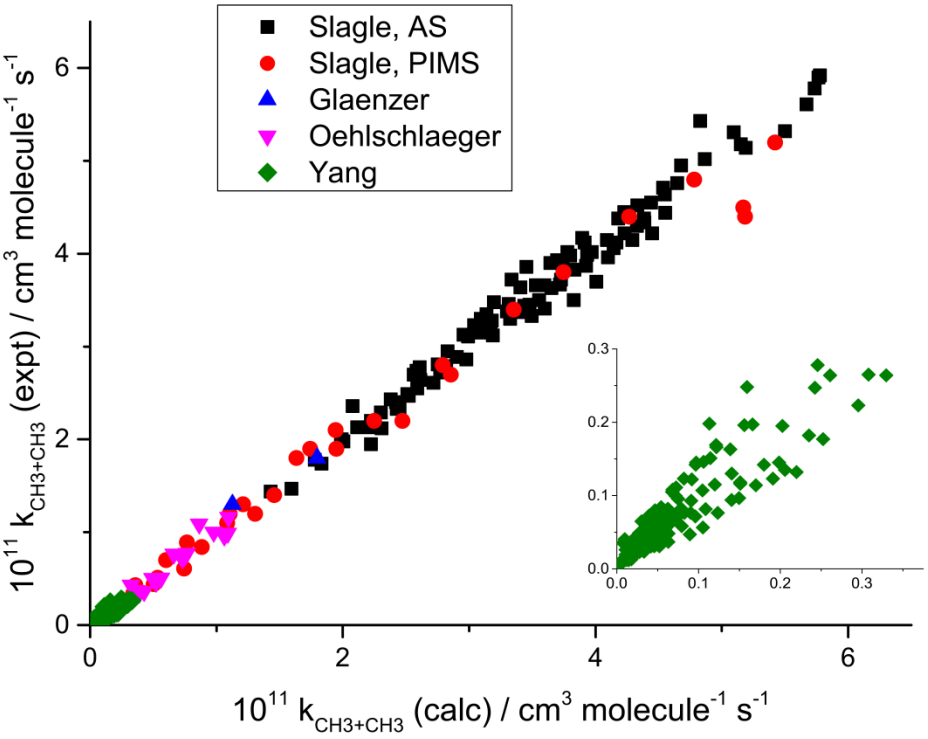

Figure S2. Plot of the experimental rate coefficients vs the best fit values from the master equation. The figure includes data in Ar (c.f. Figure S1, omitting the data of Du et al.[3]) and data in Kr (Yang et al.[6]). The Kr data have been fitted with the same ILT parameters as the Ar data, but with independent energy transfer parameters The insert shows an expanded plot for the data of Yang et al.

6. Limiting zero pressure rate coefficients, $k_0(T)$/ cm^6 molecule^{-2} s^{-1}

T/K	Fit 5	Fit 6	Baulch et al. (ref)
300	1.224E-25	8.348E-26	1.556E-26
400	2.824E-26	2.378E-26	6.614E-27
500	1.054E-26	7.845E-27	2.779E-27
600	3.354E-27	2.872E-27	1.233E-27
700	1.335E-27	1.136E-27	5.834E-28
800	5.381E-28	4.229E-28	2.937E-28
900	2.292E-28	1.890E-28	1.562E-28
1000	9.460E-29	7.461E-29	8.718E-29
1100	4.766E-29	3.630E-29	5.076E-29
1200	3.153E-29	1.808E-29	3.067E-29
1300	1.103E-29	9.175E-30	1.915E-29
1400	5.751E-30	4.746E-30	1.230E-29
1500	2.705E-30	2.488E-30	8.109E-30

Parameterized form of k_0 = A × (T/298)$^{-n}$ × exp(-C/*T*) cm^6 molecule^{-2} s^{-1}

Fit 5 (Ar) A = 1.599 × 10^{-22}
n = 10.03
C = 2191

Fit 6 (Ar) A = 1.365 × 10^{-22}
n = 10.04
C = 2227

Broadening parameters based on Troe and Ushakov[7]

For $x = k_0[\mathrm{M}]/k_\infty$,
Troe and Ushakov give $F(x) = (1 + \frac{x}{x_0})/[1 + (\frac{x}{x_0})^n]^{1/n}$
with $n = \left[\frac{\ln 2}{\ln\left(\frac{2}{F_{\mathrm{cent}}}\right)}\right][1 - b + b\left(\frac{x}{x_0}\right)^q]$
where $q = (F_{\mathrm{cent}} - 1)/\ln(\frac{F_{\mathrm{cent}}}{10})$, the parameter x_0 is in the range 0.9 – 1.1 and b is in the range 0.1 – 0.25

Fitting the fall off data from the best-fit master equation output to these expressions, with $k_\infty(T)$ and $k_0(T)$ fixed at the values derived from the master equation analysis (sections 5.1 and 5.2 in the main paper) and fitting to only $\mathrm{F_{cent}}$, b and x_0 gave the required $\mathrm{F_{cent}}$ in the form Aexp(-BT) + C with

Fit 5 (Ar) A = 0.151
B = 0.0029 K^{-1}
C = 0.0497
b = 0.25
x_0 = 1.03

Fit 6 (Ar) A = 0.135
B = 0.0022 K^{-1}
C = 0.050
b = 0.25

x_0 = 1.1

Figure S3 shows fits to the master equation output using these parameters.

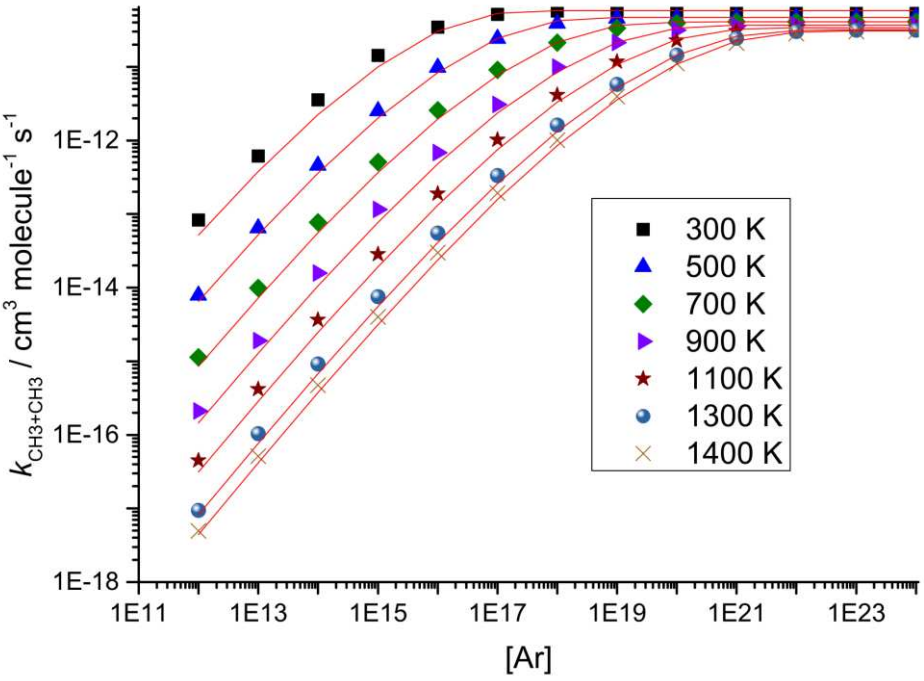

Figure S3. Comparison of the fits to the master equation output using the parameterisation of Troe and Ushakov (red lines) with the master equation output, derived from Fit 6 .

7. Chebyshev polynomials for k(p,T) for CH_3 + CH_3

This section outlines the basis of fitting the master equation output using Chebyshev polynomials. Supporting Information II is a spreadsheet that allows the rate coefficient to be calculated based on these polynomials under any pressure, temperature combination, within the fitting range. The polynomials only apply within the ranges 200 ≤ *T*/ K ≤ 2000 for Ar and 200 ≤ *T*/ K ≤ 1000 for He ; $1 \times 10^{15} \leq [M] \leq 1 \times 10^{25}$ / cm^3 molecule^{-1} s^{-1} for both Ar and He.

The Chebyshev[8] representations of the phenomenological rate coefficients are obtained using the following approach. A particular rate coefficient is represented in the form:

$$\log[\,k(T,P)] = \log[\,k(\overline{T},\overline{P})] = \sum_{i=1}^{N_T}\sum_{j=1}^{N_P}\alpha_{ij}\;\varphi_i(\overline{T})\;\varphi_j(\overline{P}) \qquad \text{(S1)}$$

where $\overline{T}$ and $\overline{P}$ are transformations of $1/T$ and $\log(P)$ on the [-1,1] interval and φ_i is a Chebyshev polynomial of degree i. In the current work N_T and N_p are chosen to be 10 and 8 respectively giving an expansion of 80 coefficients, α_{ij}, which are determined as follows:

$$\alpha_{ij} = \frac{const}{d_T d_P}\sum_{m=1}^{d_T}\sum_{n=1}^{d_P}\log[\,k(\overline{T}_{0m},\overline{P}_{on})]\varphi_i(\overline{T}_{0m})\varphi_j(\overline{P}_{0n}) \qquad \text{(S2)}$$

with

$$\overline{T}_{0m} = \cos\left[\frac{2m-1}{2d_T}\pi\right] \qquad \text{(S3)}$$

$$\overline{P}_{0m} = \cos\left[\frac{2n-1}{2d_P}\pi\right] \qquad \text{(S4)}$$

$$const = \begin{cases} 4 & i,\ j \neq 1 \\ 2 & i = 1,\ j \neq 1 \wedge i \neq 1,\ j = 1 \\ 1 & i = j = 1 \end{cases} \qquad \text{(S5)}$$

and the number of Chebyshev grid points, d_T, d_P is chosen to be 10 and 8 respectively.

In the following Tables, the rows refer to i = 1 – 10 and the columns to j = 1 – 8.

Fit 5, Ar

-10.718100	0.681445	-0.332839	0.095192	-0.018289	0.004732	0.000605	-0.001850
0.688996	-0.847133	0.307101	0.004042	-0.042774	0.010897	-0.000133	-0.000971
-0.375683	0.481882	-0.115601	-0.052401	0.031256	0.004865	-0.005578	0.000495
0.213974	-0.265188	0.033189	0.046397	-0.010502	-0.010841	0.002812	0.002058
-0.121564	0.143106	-0.002446	-0.030097	-0.001071	0.008818	0.000826	-0.002286
0.068706	-0.076154	-0.006528	0.016774	0.004906	-0.004927	-0.002484	0.001242
-0.038637	0.040084	0.007371	-0.008377	-0.004919	0.001951	0.002482	-0.000251
0.021552	-0.020837	-0.005801	0.003773	0.003669	-0.000331	-0.001774	-0.000276
-0.011794	0.010608	0.003919	-0.001504	-0.002338	-0.000307	0.001017	0.000418
0.006115	-0.005140	-0.002327	0.000504	0.001301	0.000402	-0.000479	-0.000348

Fit 6, Ar

-10.720100	0.651548	-0.325179	0.095516	-0.018035	0.004935	-0.000038	-0.001706
0.731786	-0.819788	0.311798	-0.004804	-0.042172	0.011966	-0.000308	-0.000605
-0.373495	0.460396	-0.118701	-0.048027	0.033326	0.003456	-0.006010	0.000717
0.205423	-0.249977	0.036012	0.043878	-0.012549	-0.010346	0.003620	0.001989
-0.113716	0.133118	-0.005055	-0.028653	0.000557	0.008872	0.000136	-0.002475
0.062858	-0.069902	-0.004340	0.016050	0.003696	-0.005206	-0.002037	0.001521
-0.034641	0.036317	0.005691	-0.008105	-0.004074	0.002286	0.002254	-0.000516
0.018963	-0.018653	-0.004599	0.003746	0.003118	-0.000643	-0.001694	-0.000058
-0.010200	0.009397	0.003119	-0.001580	-0.002003	-0.000056	0.001016	0.000255
0.005212	-0.004514	-0.001847	0.000595	0.001116	0.000229	-0.000504	-0.000241

Fit, average Ar: A = 5.76e-11 cm^3 $molecule^{-1}$ s^{-1} and n = -0.335, $\langle \Delta E \rangle_{\mathrm{down,ref}}$ = 295 cm^{-1}, m= 1.38, B = -1.02e-3 K^{-1}

-10.719100	0.666260	-0.328419	0.094793	-0.017968	0.004875	0.000234	-0.001761
0.712455	-0.836768	0.311040	-0.000776	-0.042379	0.011411	-0.000298	-0.000718
-0.375071	0.471736	-0.117059	-0.050572	0.032426	0.004178	-0.005788	0.000604
0.209521	-0.257209	0.034244	0.045326	-0.011474	-0.010680	0.003210	0.002044
-0.117274	0.137557	-0.003515	-0.029374	-0.000358	0.008889	0.000513	-0.002395
0.065422	-0.072554	-0.005527	0.016331	0.004372	-0.005068	-0.002288	0.001375
-0.036351	0.037861	0.006536	-0.008150	-0.004529	0.002107	0.002375	-0.000365
0.020051	-0.019526	-0.005166	0.003686	0.003402	-0.000481	-0.001724	-0.000186
-0.010862	0.009874	0.003476	-0.001491	-0.002169	-0.000179	0.000999	0.000351
0.005584	-0.004759	-0.002052	0.000519	0.001205	0.000310	-0.000475	-0.000304

Fit , average He : A = 5.76e-11 cm^3 molecule^{-1} s^{-1} and n = -0.335, $\langle \Delta E \rangle_{\mathrm{down,ref}}$ = 98 cm^{-1}, m= 1.65, 200 ≤ T/ K ≤ 1000

-1.0539E+01	4.6473E-01	-3.0248E-01	1.3893E-01	-3.6901E-02	-1.0363E-03	5.3778E-03	-2.0626E-03
2.9858E-01	-3.0155E-01	1.5403E-01	-2.7683E-02	-2.3162E-02	1.8177E-02	-1.8174E-03	-4.0888E-03
-1.0019E-01	1.2505E-01	-5.4573E-02	6.7723E-04	1.3469E-02	-4.8065E-03	-2.6131E-03	2.2318E-03
3.7660E-02	-4.9013E-02	1.7612E-02	3.6721E-03	-6.1156E-03	4.8137E-04	2.0074E-03	-5.1802E-04
-1.4585E-02	1.9122E-02	-5.6332E-03	-2.4728E-03	2.2582E-03	4.5171E-04	-9.8751E-04	-6.0191E-05
5.6310E-03	-7.2642E-03	1.6775E-03	1.2646E-03	-7.3541E-04	-3.9329E-04	3.7504E-04	1.4038E-04
-2.1732E-03	2.7203E-03	-4.6446E-04	-5.6304E-04	2.0348E-04	2.1709E-04	-1.1364E-04	-9.0528E-05
8.4180E-04	-1.0091E-03	1.1611E-04	2.3162E-04	-4.3702E-05	-9.8399E-05	2.3620E-05	4.1745E-05
-3.2748E-04	3.6971E-04	-2.4391E-05	-8.9650E-05	3.7843E-06	3.9197E-05	6.7100E-07	-1.5956E-05
1.2592E-04	-1.3124E-04	3.1803E-06	3.2502E-05	2.9106E-06	-1.4035E-05	-4.1150E-06	5.3841E-06

8. MESMER CH_3 + CH_3 xml Input File[9,10]

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    </me:HinderedRotorPotential>
                <me:periodicity>3</me:periodicity>
  </me:ExtraDOSCMethod>

  <me:energyTransferModel xsi:type="me:ExponentialDown">


        <me:deltaEDown bathGas="Ar" units="cm-1" >295</me:deltaEDown>
                <me:deltaEDownTExponent bathGas="Ar" referenceTemperature="1400"
>1.38</me:deltaEDownTExponent>
                 <me:deltaEDownActivationParam units="K-1" >-
0.00102</me:deltaEDownActivationParam>


     <me:deltaEDown bathGas="He" units="cm-1" lower="50" upper="400"
stepsize="10">98</me:deltaEDown>
     <me:deltaEDownTExponent bathGas="He" lower="-2.5" upper="2.5"
stepsize="0.01">1.65</me:deltaEDownTExponent>



   </me:energyTransferModel>
   <me:reservoirSize units="kJ/mol">-250.0</me:reservoirSize>
  </molecule>

  <molecule id="N2">
   <atom elementType="N"/>
   <propertyList>
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    <scalar>48.0</scalar>
   </property>
   <property dictRef="me:sigma">
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   <property dictRef="me:MW">
    <scalar units="amu">28.0</scalar>
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  </propertyList>
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<molecule id="He">
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  <propertyList>
   <property dictRef="me:epsilon">
    <scalar>10.22</scalar>
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   <property dictRef="me:sigma">
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   <property dictRef="me:MW">
    <scalar>4.04</scalar>
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<molecule id="Ar">
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  <propertyList>
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   <property dictRef="me:sigma">
    <scalar>3.47</scalar>
   </property>
   <property dictRef="me:MW">
    <scalar>39.948</scalar>
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  </propertyList>
</molecule>

<molecule id="Kr">
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    <scalar>159.0</scalar>
   </property>
   <property dictRef="me:sigma">
    <scalar>3.75</scalar>
   </property>
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      </property>
     </propertyList>
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  </moleculeList>
  <reactionList>
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    <reactant>
     <molecule ref="CH3" role="excessReactant" />
    </reactant>
    <product>
     <molecule ref="C2H6" role="modelled"/>
    </product>
    <me:excessReactantConc>1e14</me:excessReactantConc>

   <me:MCRCMethod name="MesmerILT" xsi:type="MesmerILT">
    <!--me:preExponential>5.93e-11</me:preExponential-->
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11</me:preExponential>
    <me:activationEnergy>0.0</me:activationEnergy>
    <me:TInfinity>298.0</me:TInfinity>
    <!--me:nInfinity>-0.2518</me:nInfinity-->
          <me:nInfinity lower="-0.9" upper="0.9" stepsize="0.005">-0.335</me:nInfinity>
          </me:MCRCMethod>


   </reaction>
  </reactionList>
  <me:conditions>
   <me:bathGas>Ar</me:bathGas>
   <me:PTs>


<me:PTpair       units="atm" P= "          2.19E-01          " T= "    1803    " precision="d">
          <me:bathGas>Ar</me:bathGas>                                          </me:PTpair>


   </me:PTs>
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  <me:modelParameters>
   <me:grainSize units="cm-1">50</me:grainSize>
   <me:energyAboveTheTopHill>20.</me:energyAboveTheTopHill>
  </me:modelParameters>
   <me:control>
   <!--me:calcMethod xsi:type="me:marquardt">
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    <me:MarquardtTolerance>1e-7</me:MarquardtTolerance>
    <me:MarquardtDerivDelta>0.025</me:MarquardtDerivDelta>
   </me:calcMethod-->
   <me:testDOS/>
         <me:printSpeciesProfile />
   <me:testMicroRates/>
   <!--<me:printGrainDOS />-->
   <!--<me:printCellDOS />-->
   <!--<me:printReactionOperatorColumnSums />-->
   <me:printGrainkfE/>
   <!--<me:printGrainBoltzmann />-->
   <me:printGrainkbE/>
   <me:printSpeciesProfile/>
   <me:testRateConstants/>
         <me:calcMethod xsi:type="me:analyticalRepresentation">
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    <me:chebNumConc>9</me:chebNumConc>
    <me:chebMaxTemp>2000</me:chebMaxTemp>
    <me:chebMinTemp>200</me:chebMinTemp>
    <me:chebMaxConc units="PPCC">1E+25</me:chebMaxConc>
    <me:chebMinConc>1E+15</me:chebMinConc>
    <me:chebTExSize>10</me:chebTExSize>
    <me:chebPExSize>8</me:chebPExSize>
   </me:calcMethod>
   <me:eigenvalues>1</me:eigenvalues>
  </me:control>
</me:mesmer>
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