Supporting Information

Experimental Evidence of Dioxole Unimolecular Decay Pathway for Isoprene-Derived Criegee Intermediates

Michael F. Vansco[1], Rebecca L. Caravan[2,3,4], Kristen Zuraski[2], Frank A. F. Winiberg[5,6], Kendrew Au[3], Nisalak Trongsiriwat[1], Patrick J. Walsh[1], David L. Osborn[3], Carl J. Percival[4], M. Anwar H. Khan[7], Dudley E. Shallcross[7], Craig A. Taatjes[3*], and Marsha I. Lester[1**]

[1]Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, USA.
[2]NASA Postdoctoral Program Fellow, NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA.
[3]Combustion Research Facility, Mailstop 9055, Sandia National Laboratories, Livermore, CA 94551, USA.
[4]Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA.
[5]NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA.
[6]California Institute of Technology, Pasadena, CA 91125, USA.
[7]School of Chemistry, Cantock's Close, University of Bristol, Bristol BS8 1TS, UK.

[*] Corresponding author email: cataatj@sandia.gov
[**]Corresponding author email: milester@sas.upenn.edu

Table of Contents:

Section S1. Theoretical calculations

Additional calculations were carried out to supplement the results of previous theoretical studies in cases where the energies of specific products were not reported. Kuwata *et al*.[1] reported the unimolecular decay of the *syn*-MACR-oxide Criegee intermediate via the dioxole channel (Scheme 4). C-C bond fission of methylmalonaldehyde was not investigated. We carried out theoretical calculations of methylmalonaldehyde and the predicted alkyl radical products (2-methyl-vinoxy and formyl radical) to demonstrate that sufficient energy is available for C-C bond fission. The energy in Scheme 4 is reported at the same level of theory used by Kuwata *et al*.[1] (CBS/QB3//B3LYP/6-311G(d,p)), including harmonic zero point energy (ZPE) corrections. The stationary point geometry of methylmalonaldehyde, 2-methyl-vinoxy radical, and formyl radical are reported in Table S1 and the relative energies are reported in Table S2.

The acetyl radical + O_2 reaction was theoretically investigated by Carr *et al*.[2] In this study, the barrier to the formaldehyde products from the decomposition of α-lactone was reported, but not the asymptotic product energy. We carried out theoretical calculations to demonstrate that formaldehyde + OH + CO is the thermodynamically favored product. The energy in Scheme 5 for formaldehyde + OH + CO is reported at the CCSD/cc-pVTZ//B2PLYP-D3/cc-pVTZ level of theory relative to α-lactone + OH, including harmonic ZPE corrections. The stationary point geometry of α-lactone, OH, CO, and formaldehyde are reported in Table S1; the relative energies are reported in Table S2.

Table S1. Stationary point geometries of species discussed in Section S3.

Stationary Point Geometries			
Minima			
methyl-malonaldehyde[a]			
C	-0.75902	1.59477	-0.00040
H	-0.97651	1.58207	-1.06702
H	-1.70979	1.64517	0.52282
H	-0.18862	2.49388	0.22592
C	0.01060	0.35087	0.40497
H	0.24354	0.34149	1.47439
C	1.34846	0.20971	-0.30109
H	1.49592	0.87823	-1.16991
O	2.19247	-0.58912	0.02410
C	-0.77023	-0.93498	0.15931
H	-0.21731	-1.85719	0.40461
O	-1.89573	-0.96161	-0.27004
2-methyl-vinoxy radical[a]			
C	-1.50101	-0.41221	0.00012
H	-2.15872	-0.34593	0.87596
H	-0.99984	-1.37982	0.00146
H	-2.15679	-0.34783	-0.87742
C	-0.50778	0.67815	-0.00014
H	-0.85153	1.72006	-0.00028
C	0.90245	0.45293	0.00007
H	1.54651	1.35270	0.00048
O	1.40790	-0.67231	-0.00006
formyl radical[a]			
C	0.06231	0.58418	0.00000
H	-0.87235	1.21503	0.00000
O	0.06231	-0.59001	0.00000
α-lactone[b]			
C	-1.02255	0.59518	0.00008
H	-1.49203	0.90431	-0.92253
H	-1.49234	0.90466	0.92204
C	0.32406	0.06797	0.00048
O	-0.61119	-0.88163	-0.00006
O	1.50809	0.15815	-0.00018
OH[b]			
O	0.00000	0.00000	0.10786
H	0.00000	0.00000	-0.86290

Formaldehyde[b]			
C	-0.00001	0.52883	0.00000
H	0.93516	1.11372	0.00000
H	-0.93505	1.11393	0.00000
O	-0.00001	-0.67508	0.00000
CO[b]			
C	0.00000	0.00000	-0.64654
O	0.00000	0.00000	0.48490

[a]B3LYP/6-311G(d,p)
[b]B2PLYP-D3/cc-pVTZ

Table S2. Calculated energies and ZPE corrections of predicted product asymptotes.

Species	Relative Energy (kcal mol^{-1})	Relative ZPE (kcal mol^{-1})	Total Energy (kcal mol^{-1})
methyl-malonaldehyde[a]	0	0	0
2-methyl-vinoxy + formyl radical[a]	70.4	-5.7	64.7
α-lactone + OH[b]	0	0	0
formaldehyde + OH + CO[b]	-10.9	-4.3	-15.2

[a]CBS/QB3//B3LYP/6-311G(d,p)
[b]CCSD/cc-pVTZ//B2PLYP-D3/cc-pVTZ

Section S2. Product branching analysis

For the product branching analysis, the PIE curves that are analyzed are obtained by integrating over the full product mass and time window (0-80 ms). The known absolute photoionization spectra of the products are scaled to match the experimental PIE curves via a least squares method.[3-6] Examples are shown in the main text for mass channels where only the products contribute to the photoionization signal (Figures 1, 5, 6). For ketene (m/z 42) and glyoxal products (m/z 58), interfering species contribute to the photoionization signal of the associated mass channel (Figures 2 and 4). The interfering species have the same nominal mass but different numbers of C and O atoms that results in partially resolved features in the mass spectrum. The photoionization spectra of the interfering species are required to quantify the contribution of ketene and glyoxal in their respective PIE curve (m/z 42 and m/z 58, respectively). The mass resolution of the MPIMS experiment is sufficient to estimate the photoionization spectrum of each interfering species by integrating over a mass region where it is the dominant spectral carrier. An example is shown in Figure 3 of the main text for the ketene (m/z 42) product channel. Integration over the 42.04-42.08 mass region results in an estimated photoionization spectrum of the interfering species. The contributions to the PIE curve of the full m/z 42 mass and time window (Figure S1, open circles) can then be separated by a scaled sum (black line) of the absolute photoionization spectrum of ketene (green line)[4] and the estimated photoionization spectrum of the interfering species (blue line) by a least squares method to extract branching information for the ketene product channel.

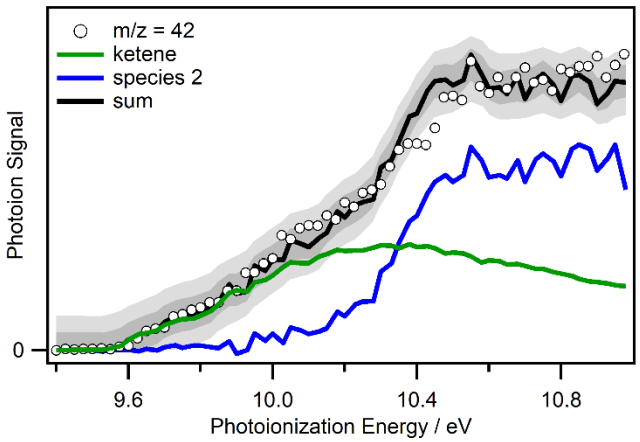

Figure S1. PIE curve of m/z 42 (open circles) integrated over the full kinetic time window (0-80 ms) and mass window (41.95-42.08 amu). The black lines shows the result of a least squares fit of the absolute photoionization spectrum of ketene and experimental photoionization spectrum of the interfering species (species 2) to the m/z 42 PIE curve. The darker and lighter grey shaded regions represents 1σ and 2σ uncertainty in the fit, respectively.

For the glyoxal product channel, the same analysis was conducted to estimate the photoionization spectrum of the interfering species (Figure S2) and determine branching to the glyoxal product channel (Figure S3). The identity of the interfering specie(s) is unknown. The chemical composition is consistent with acetone (IE = 9.70 eV)[7] or 2-propen-1-ol (IE = 9.70 eV).[8] However, photoionization signal is observed at lower ionization energies, potentially due to a daughter ion.

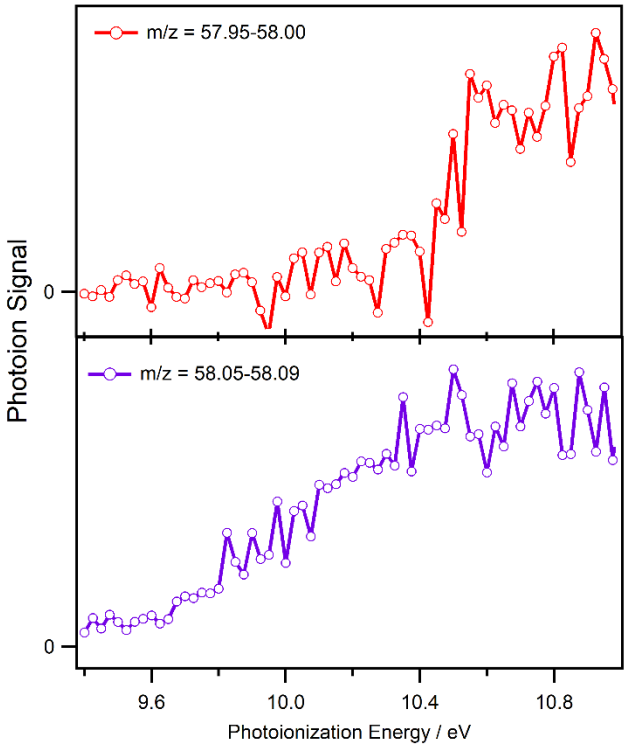

Figure S2. (Top) The PIE curve of the 57.95-58.00 mass window (red open circles) is consistent with the known PI spectrum of glyoxal.[4] (Lower panel) PIE curve associated with the 58.05-58.09 mass window (purple open circles). The PIE curves are generated by integrating over the full kinetic time window (0-80 ms).

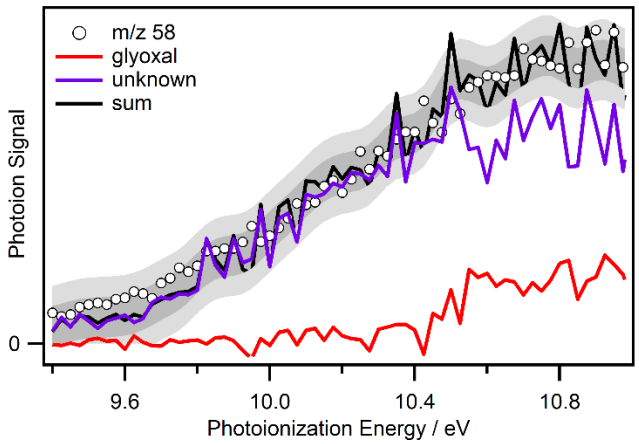

Figure S3. PIE curve of m/z 58 (open circles) integrated over the full kinetic time window (0-80 ms) and mass window (57.95-58.09 amu). The black lines shows the result of a least squares fit of the absolute photoionization spectrum of glyoxal and experimental photoionization spectrum of the interfering species (unknown) to the m/z 58 PIE curve. The darker and lighter grey shaded regions represents 1σ and 2σ uncertainty in the fit, respectively.

In this case, an assumption of the photoionization cross section of glyoxal is required because only the relative photoionization spectrum of glyoxal is known.[5] We estimate the photoionization cross-section of glyoxal by drawing comparisons to similar molecules with known absolute spectra. Acrolein is chemically similar to glyoxal, only differing by a C=C vs C=O bond, respectively. It is well known that the photoionization cross section of molecules with C=O bonds are larger than those with C=C bonds.[9] For example, the photoionization cross section of formaldehyde (H_2CO) at 11 eV is ca. 20% greater than that of ethylene (C_2H_4).[3, 10] Thus, to account for the difference in structure we scale the photoionization spectrum of glyoxal such that its cross-section at 11 eV is 20% greater than that of acrolein.[6] The overall product branching is insensitive to the 20% change in the cross-section (± 1 %) used for the analysis of glyoxal on the m/z 58 mass channel and is within uncertainty of the analysis.

Section S3. MESMER input files

The parameters used for the master equation modeling using the Master Equation Solver for Multi-Energy well Reactions (MESMER) are described briefly; the input files for the calculations are also provided below. Collisional energy transfer was described using an exponential down model ΔE_{down} = 130 cm^{-1} in N_2. Lennard-Jones parameters were chosen based on those determined for similar molecules.[2] Parameters from the high level electronic structure calculations carried out by Weidman *et al*.[11] and Davis *et al*.[12] were used as inputs for the vinoxy + O_2 and 2-methyl-vinoxy + O_2 simulations, respectively. This includes the energetics for each stationary point and vibrational frequencies. The inputs for the rotational constants of each species were calculated at the CCSD(T)/cc-pVTZ level of theory using the stationary point geometries previously calculated.[11-12]

Vinoxy radical + O_2

```
<?xml version="1.0" encoding="utf-8" ?>
<?xml-stylesheet type='text/xsl' href='../../mesmer2.xsl' media='other'?>
<?xml-stylesheet type='text/xsl' href='../../mesmer1.xsl' media='screen'?>
<me:mesmer xmlns="http://www.xml-cml.org/schema"
        xmlns:me="http://www.chem.leeds.ac.uk/mesmer"
        xmlns:xsi="http://www.w3.org/2001/XMLSchema-instance">
 <me:title> Vinoxy O2 Association</me:title>
 <moleculeList>
  <molecule id="vinoxy" description="CH2CHO">
   <atomArray>
    <atom id="a1" elementType="C" />
    <atom id="a2" elementType="C" />
    <atom id="a3" elementType="H" />
    <atom id="a4" elementType="H" />
    <atom id="a5" elementType="O" />
    <atom id="a6" elementType="H" />
   </atomArray>
   <bondArray>
    <bond atomRefs2="a1 a2" order="1" />
    <bond atomRefs2="a1 a3" order="1" />
    <bond atomRefs2="a1 a4" order="1" />
    <bond atomRefs2="a2 a5" order="2" />
    <bond atomRefs2="a2 a6" order="1" />
   </bondArray>
```

```
    <propertyList>
      <property dictRef="me:ZPE">
        <scalar units="kcal/mol">0</scalar>
      </property>
      <property dictRef="me:rotConsts">
        <array units="cm-1">2.232601 0.380527 0.325114</array>
      </property>
      <property dictRef="me:symmetryNumber">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:frequenciesScaleFactor">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:vibFreqs">
        <array units="cm-1">3277 3159 2988 1573 1474 1403 1158 970 499 974 735 432
</array>
      </property>
      <property dictRef="me:MW">
        <scalar units="amu">43</scalar>
      </property>
      <property dictRef="me:spinMultiplicity">
        <scalar>2</scalar>
      </property>
    </propertyList>
    <me:DOSCMethod xsi:type="ClassicalRotors"/>
  </molecule>
  <molecule id="O2" description="oxygen">
    <atomArray>
      <atom id="a1" elementType="O" />
      <atom id="a2" elementType="O" />
    </atomArray>
    <bondArray>
      <bond atomRefs2="a1 a2" order="2" />
    </bondArray>
    <propertyList>
      <property dictRef="me:ZPE">
        <scalar units="kcal/mol">0.0</scalar>
      </property>
      <property dictRef="me:rotConsts">
        <array units="cm-1">1.431782</array>
      </property>
      <property dictRef="me:symmetryNumber">
        <scalar>2</scalar>
      </property>
      <property dictRef="me:frequenciesScaleFactor">
        <scalar>1</scalar>
```

```
    </property>
    <property dictRef="me:vibFreqs">
      <array units="cm-1">1583</array>
    </property>
    <property dictRef="me:MW">
      <scalar units="amu">32</scalar>
    </property>
    <property dictRef="me:spinMultiplicity">
      <scalar>3</scalar>
    </property>
  </propertyList>
  <me:DOSCMethod xsi:type="ClassicalRotors"/>
</molecule>
<molecule id="OH" description="OH radical">
  <atomArray>
    <atom id="a1" elementType="O" />
    <atom id="a2" elementType="H" />
  </atomArray>
  <bondArray>
    <bond atomRefs2="a1 a2" order="1" />
  </bondArray>
  <propertyList>
    <property dictRef="me:ZPE">
      <scalar units="kcal/mol">0.0</scalar>
    </property>
    <property dictRef="me:rotConsts">
      <array units="cm-1">18.86743</array>
    </property>
    <property dictRef="me:symmetryNumber">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:vibFreqs">
      <array units="cm-1">3718</array>
    </property>
    <property dictRef="me:MW">
      <scalar units="amu">17</scalar>
    </property>
    <property dictRef="me:spinMultiplicity">
      <scalar>2</scalar>
    </property>
    <property dictRef="me:eletronicExcitation">
      <array units="cm-1">139.7</array>
    </property>
```

```
    </propertyList>
    <me:DOSCMethod xsi:type="ClassicalRotors"/>
   </molecule>
   <molecule id="PRa" description="peroxy vinoxy O2 adduct">
    <atomArray>
     <atom id="a1" elementType="C" />
     <atom id="a2" elementType="C" />
     <atom id="a3" elementType="O" />
     <atom id="a4" elementType="H" />
     <atom id="a5" elementType="O" />
     <atom id="a6" elementType="O" />
     <atom id="a7" elementType="H" />
     <atom id="a8" elementType="H" />
    </atomArray>
    <bondArray>
     <bond atomRefs2="a1 a2" order="1" />
     <bond atomRefs2="a1 a7" order="1" />
     <bond atomRefs2="a1 a8" order="1" />
     <bond atomRefs2="a1 a5" order="1" />
     <bond atomRefs2="a2 a3" order="2" />
     <bond atomRefs2="a2 a4" order="1" />
     <bond atomRefs2="a5 a6" order="1" />
    </bondArray>
    <propertyList>
     <property dictRef="me:ZPE">
      <scalar units="kcal/mol">-21.9</scalar>
     </property>
     <property dictRef="me:rotConsts">
      <array units="cm-1">0.552028 0.099531 0.089599</array>
     </property>
     <property dictRef="me:symmetryNumber">
      <scalar>1</scalar>
     </property>
     <property dictRef="me:frequenciesScaleFactor">
      <scalar>1</scalar>
     </property>
     <property dictRef="me:vibFreqs">
      <array units="cm-1">3150 3084 2977 1789 1451 1408 1333 1258 1145 1107 1046 969
742 584 439 295 148 54</array>
     </property>
     <property dictRef="me:MW">
      <scalar units="amu">75</scalar>
     </property>
     <property dictRef="me:spinMultiplicity">
      <scalar>2</scalar>
     </property>
```

```
    <property dictRef="me:epsilon">
      <scalar>473.17</scalar>
    </property>
    <property dictRef="me:sigma">
      <scalar>5.09</scalar>
    </property>
  </propertyList>
  <me:energyTransferModel xsi:type="me:ExponentialDown">
    <me:deltaEDown units="cm-1">130</me:deltaEDown>
  </me:energyTransferModel>
  <me:DOSCMethod xsi:type="ClassicalRotors"/>
</molecule>
<molecule id="TS1" description="TS1a: PRa -> QR1">
  <atomArray>
    <atom id="a1" elementType="C" />
    <atom id="a2" elementType="C" />
    <atom id="a3" elementType="O" />
    <atom id="a4" elementType="O" />
    <atom id="a5" elementType="O" />
    <atom id="a6" elementType="H" />
    <atom id="a7" elementType="H" />
    <atom id="a8" elementType="H" />
  </atomArray>
  <bondArray>
    <bond atomRefs2="a1 a2" order="1" />
    <bond atomRefs2="a1 a4" order="1" />
    <bond atomRefs2="a1 a6" order="1" />
    <bond atomRefs2="a1 a7" order="1" />
    <bond atomRefs2="a4 a5" order="1" />
                <bond atomRefs2="a2 a3" order="2" />
                <bond atomRefs2="a2 a8" order="1" />
  </bondArray>
  <propertyList>
    <property dictRef="me:ZPE">
      <scalar units="kcal/mol">-0.7</scalar>
    </property>
    <property dictRef="me:rotConsts">
      <array units="cm-1">0.444475 0.122314 0.099436</array>
    </property>
    <property dictRef="me:symmetryNumber">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:vibFreqs">
```

```
      <array units="cm-1">3151 3044 1921 1829 1453 1272 1221 1156 1046 929 885 797 682
538 395 380 184</array>
     </property>
     <property dictRef="me:MW">
      <scalar units="amu">75</scalar>
     </property>
     <property dictRef="me:spinMultiplicity">
      <scalar>2</scalar>
     </property>
     <property dictRef="me:imFreqs">
      <scalar units="cm-1">2130</scalar>
     </property>
    </propertyList>
    <me:DOSCMethod xsi:type="ClassicalRotors"/>
   </molecule>
   <molecule id="TS2" description="PRa -> QR2">
    <atomArray>
     <atom id="a1" elementType="C" />
     <atom id="a2" elementType="C" />
     <atom id="a3" elementType="O" />
     <atom id="a4" elementType="H" />
     <atom id="a5" elementType="O" />
     <atom id="a6" elementType="H" />
     <atom id="a7" elementType="H" />
     <atom id="a8" elementType="O" />
    </atomArray>
    <bondArray>
     <bond atomRefs2="a1 a2" order="1" />
     <bond atomRefs2="a1 a5" order="1" />
     <bond atomRefs2="a1 a7" order="1" />
     <bond atomRefs2="a1 a6" order="1" />
     <bond atomRefs2="a5 a8" order="1" />
                <bond atomRefs2="a2 a4" order="1" />
                <bond atomRefs2="a2 a3" order="2" />
    </bondArray>
    <propertyList>
     <property dictRef="me:ZPE">
      <scalar units="kcal/mol">16.8</scalar>
     </property>
     <property dictRef="me:rotConsts">
      <array units="cm-1">0.619707 0.093273 0.089574</array>
     </property>
     <property dictRef="me:symmetryNumber">
      <scalar>1</scalar>
     </property>
     <property dictRef="me:frequenciesScaleFactor">
```

```
      <scalar>1</scalar>
     </property>
     <property dictRef="me:vibFreqs">
      <array units="cm-1">3138 2992 1992 1758 1400 1288 1134 1091 1085 1022 793 743 640
493 328 138 120 </array>
     </property>
     <property dictRef="me:MW">
      <scalar units="amu">75</scalar>
     </property>
     <property dictRef="me:spinMultiplicity">
      <scalar>2</scalar>
     </property>
     <property dictRef="me:imFreqs">
      <scalar units="cm-1">1897</scalar>
     </property>
    </propertyList>
    <me:DOSCMethod xsi:type="ClassicalRotors"/>
   </molecule>
   <molecule id="ketene" description="CH2CO">
    <atomArray>
     <atom id="a1" elementType="C" />
     <atom id="a2" elementType="O" />
     <atom id="a3" elementType="C" />
     <atom id="a4" elementType="H" />
     <atom id="a5" elementType="H" />
    </atomArray>
    <bondArray>
     <bond atomRefs2="a1 a3" order="2" />
     <bond atomRefs2="a1 a2" order="2" />
     <bond atomRefs2="a3 a4" order="1" />
     <bond atomRefs2="a3 a5" order="1" />
    </bondArray>
    <propertyList>
     <property dictRef="me:ZPE">
      <scalar units="kcal/mol">-12.6</scalar>
     </property>
     <property dictRef="me:rotConsts">
      <array units="cm-1">9.428139 0.341214 0.329295</array>
     </property>
     <property dictRef="me:symmetryNumber">
      <scalar>1</scalar>
     </property>
     <property dictRef="me:frequenciesScaleFactor">
      <scalar>1</scalar>
     </property>
     <property dictRef="me:vibFreqs">
```

```
      <array units="cm-1">3307 3202 2202 1413 1152 991 595 522 436 </array>
    </property>
    <property dictRef="me:MW">
      <scalar units="amu">42</scalar>
    </property>
    <property dictRef="me:spinMultiplicity">
      <scalar>1</scalar>
    </property>
  </propertyList>
  <me:DOSCMethod xsi:type="ClassicalRotors"/>
</molecule>
<molecule id="HO2">
  <atomArray>
    <atom id="a1" elementType="O" />
    <atom id="a2" elementType="H" />
    <atom id="a3" elementType="O" />
  </atomArray>
  <bondArray>
    <bond atomRefs2="a1 a2" order="1" />
    <bond atomRefs2="a1 a3" order="1" />
  </bondArray>
  <propertyList>
    <property dictRef="me:ZPE">
      <scalar units="kcal/mol">0.0</scalar>
    </property>
    <property dictRef="me:rotConsts">
      <array units="cm-1">20.52618 1.113085 1.05583</array>
    </property>
    <property dictRef="me:symmetryNumber">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:vibFreqs">
      <array units="cm-1">3674 1434 1126</array>
    </property>
    <property dictRef="me:MW">
      <scalar units="amu">33</scalar>
    </property>
    <property dictRef="me:spinMultiplicity">
      <scalar>2</scalar>
    </property>
  </propertyList>
  <me:DOSCMethod xsi:type="ClassicalRotors"/>
</molecule>
```

```
  <molecule id="QR1" description="peroxide_isomer_opt">
   <atomArray>
    <atom id="a1" elementType="C" />
    <atom id="a2" elementType="C" />
    <atom id="a3" elementType="O" />
    <atom id="a4" elementType="H" />
    <atom id="a5" elementType="H" />
    <atom id="a6" elementType="O" />
    <atom id="a7" elementType="H" />
    <atom id="a8" elementType="O" />
   </atomArray>
   <bondArray>
    <bond atomRefs2="a1 a2" order="1" />
    <bond atomRefs2="a1 a5" order="1" />
    <bond atomRefs2="a1 a4" order="1" />
    <bond atomRefs2="a1 a3" order="1" />
    <bond atomRefs2="a3 a6" order="1" />
    <bond atomRefs2="a6 a7" order="1" />
    <bond atomRefs2="a2 a8" order="2" />
   </bondArray>
   <propertyList>
    <property dictRef="me:ZPE">
     <scalar units="kcal/mol">-21.0</scalar>
    </property>
    <property dictRef="me:rotConsts">
     <array units="cm-1">0.316736 0.148749 0.112639</array>
    </property>
    <property dictRef="me:symmetryNumber">
     <scalar>1</scalar>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
     <scalar>1</scalar>
    </property>
    <property dictRef="me:vibFreqs">
     <array units="cm-1">3743 3130 3062 1894 1428 1397 1341 1275 1062 936 844 814 706
424 378 272 206 144</array>
    </property>
    <property dictRef="me:MW">
     <scalar units="amu">75</scalar>
    </property>
    <property dictRef="me:spinMultiplicity">
     <scalar>2</scalar>
    </property>
    <property dictRef="me:epsilon">
     <scalar>473.17</scalar>
    </property>
```

```
      <property dictRef="me:sigma">
        <scalar>5.09</scalar>
      </property>
    </propertyList>
    <me:energyTransferModel xsi:type="me:ExponentialDown">
      <me:deltaEDown units="cm-1">130</me:deltaEDown>
    </me:energyTransferModel>
    <me:DOSCMethod xsi:type="ClassicalRotors"/>
  </molecule>
  <molecule id="TS4" description="TS QR1 -> CH2OOH_CO">
    <atomArray>
      <atom id="a1" elementType="C" />
      <atom id="a2" elementType="C" />
      <atom id="a3" elementType="O" />
      <atom id="a4" elementType="H" />
      <atom id="a5" elementType="H" />
      <atom id="a6" elementType="O" />
      <atom id="a7" elementType="H" />
      <atom id="a8" elementType="O" />
    </atomArray>
    <bondArray>
      <bond atomRefs2="a1 a3" order="1" />
      <bond atomRefs2="a1 a5" order="1" />
      <bond atomRefs2="a3 a6" order="1" />
      <bond atomRefs2="a6 a7" order="1" />
      <bond atomRefs2="a1 a4" order="1" />
      <bond atomRefs2="a2 a8" order="2" />
    </bondArray>
    <propertyList>
      <property dictRef="me:ZPE">
        <scalar units="kcal/mol">-9.7</scalar>
      </property>
      <property dictRef="me:rotConsts">
        <array units="cm-1">0.295498 0.127205 0.098056</array>
      </property>
      <property dictRef="me:symmetryNumber">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:frequenciesScaleFactor">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:vibFreqs">
        <array units="cm-1">3745 3251 3121 1964 1441 1393 1209 1144 973 846 605 477 364
323 200 134 99</array>
      </property>
      <property dictRef="me:MW">
```

```
      <scalar units="amu">75</scalar>
     </property>
     <property dictRef="me:spinMultiplicity">
      <scalar>2</scalar>
     </property>
     <property dictRef="me:imFreqs">
      <scalar units="cm-1">375</scalar>
     </property>
    </propertyList>
    <me:DOSCMethod xsi:type="ClassicalRotors"/>
   </molecule>
        <molecule id="TS5" description="TS QR1 -> ketene_HO2">
    <atomArray>
     <atom id="a1" elementType="O" />
     <atom id="a2" elementType="O" />
     <atom id="a3" elementType="H" />
     <atom id="a4" elementType="C" />
     <atom id="a5" elementType="H" />
     <atom id="a6" elementType="H" />
     <atom id="a7" elementType="C" />
     <atom id="a8" elementType="O" />
    </atomArray>
    <bondArray>
     <bond atomRefs2="a4 a5" order="1" />
     <bond atomRefs2="a4 a6" order="1" />
     <bond atomRefs2="a4 a7" order="1" />
     <bond atomRefs2="a7 a8" order="1" />
     <bond atomRefs2="a1 a2" order="1" />
     <bond atomRefs2="a2 a3" order="1" />
    </bondArray>
    <propertyList>
     <property dictRef="me:ZPE">
      <scalar units="kcal/mol">2.1</scalar>
     </property>
     <property dictRef="me:rotConsts">
      <array units="cm-1">0.326465 0.105935 0.085832</array>
     </property>
     <property dictRef="me:symmetryNumber">
      <scalar>1</scalar>
     </property>
     <property dictRef="me:frequenciesScaleFactor">
      <scalar>1</scalar>
     </property>
     <property dictRef="me:vibFreqs">
      <array units="cm-1">3754 3254 3159 2119 1399 1376 1056 1051 944 847 653 445 424
406 266 131 50</array>
```

```
    </property>
    <property dictRef="me:MW">
      <scalar units="amu">75</scalar>
    </property>
    <property dictRef="me:spinMultiplicity">
      <scalar>2</scalar>
    </property>
    <property dictRef="me:imFreqs">
      <scalar units="cm-1">695</scalar>
    </property>
  </propertyList>
  <me:DOSCMethod xsi:type="ClassicalRotors"/>
</molecule>
<molecule id="H2CO">
  <atomArray>
    <atom id="a1" elementType="C" />
    <atom id="a2" elementType="O" />
    <atom id="a3" elementType="H" />
    <atom id="a4" elementType="H" />
  </atomArray>
  <bondArray>
    <bond atomRefs2="a1 a2" order="1" />
    <bond atomRefs2="a1 a3" order="1" />
    <bond atomRefs2="a1 a4" order="1" />
  </bondArray>
  <propertyList>
    <property dictRef="me:ZPE">
      <scalar units="kcal/mol">-50.1</scalar>
    </property>
    <property dictRef="me:rotConsts">
      <array units="cm-1">9.522858 1.287951 1.13451</array>
    </property>
    <property dictRef="me:symmetryNumber">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:vibFreqs">
      <array units="cm-1">3004 2937 1773 1537 1272 1188</array>
    </property>
    <property dictRef="me:MW">
      <scalar units="amu">30</scalar>
    </property>
    <property dictRef="me:spinMultiplicity">
      <scalar>1</scalar>
```

```
    </property>
                <property dictRef="me:epsilon">
      <scalar>473.17</scalar>
    </property>
    <property dictRef="me:sigma">
      <scalar>5.09</scalar>
    </property>
   </propertyList>
   <me:energyTransferModel xsi:type="me:ExponentialDown">
    <me:deltaEDown units="cm-1">130</me:deltaEDown>
   </me:energyTransferModel>
   <me:DOSCMethod xsi:type="ClassicalRotors"/>
  </molecule>
      <molecule id="CH2OOH">
   <atomArray>
    <atom id="a1" elementType="C" />
    <atom id="a2" elementType="H" />
    <atom id="a3" elementType="H" />
    <atom id="a4" elementType="O" />
                <atom id="a5" elementType="O" />
                <atom id="a6" elementType="H" />
   </atomArray>
   <bondArray>
    <bond atomRefs2="a1 a2" order="1" />
    <bond atomRefs2="a1 a3" order="1" />
    <bond atomRefs2="a1 a4" order="1" />
                <bond atomRefs2="a4 a5" order="1" />
                <bond atomRefs2="a5 a6" order="1" />
   </bondArray>
   <propertyList>
    <property dictRef="me:ZPE">
      <scalar units="kcal/mol">-15.1</scalar>
    </property>
    <property dictRef="me:rotConsts">
      <array units="cm-1">1.730428 0.376788 0.321947</array>
    </property>
    <property dictRef="me:symmetryNumber">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:vibFreqs">
      <array units="cm-1">3774 3284 3142 1441 1372 1204 1149 840 709 484 275
176</array>
    </property>
```

```
    <property dictRef="me:MW">
      <scalar units="amu">47</scalar>
    </property>
    <property dictRef="me:spinMultiplicity">
      <scalar>2</scalar>
    </property>
  </propertyList>
  <me:DOSCMethod xsi:type="ClassicalRotors"/>
</molecule>
       <molecule id="CO">
  <atomArray>
    <atom id="a1" elementType="C" />
    <atom id="a2" elementType="O" />
  </atomArray>
  <bondArray>
    <bond atomRefs2="a1 a2" order="2" />
  </bondArray>
  <propertyList>
    <property dictRef="me:ZPE">
      <scalar units="kcal/mol">0</scalar>
    </property>
    <property dictRef="me:rotConsts">
      <array units="cm-1">1.905061</array>
    </property>
    <property dictRef="me:symmetryNumber">
      <scalar>2</scalar>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:vibFreqs">
      <array units="cm-1">2146</array>
    </property>
    <property dictRef="me:MW">
      <scalar units="amu">28</scalar>
    </property>
    <property dictRef="me:spinMultiplicity">
      <scalar>1</scalar>
    </property>
  </propertyList>
  <me:DOSCMethod xsi:type="ClassicalRotors"/>
</molecule>
       <molecule id="QR2">
  <atomArray>
    <atom id="a1" elementType="C" />
    <atom id="a2" elementType="C" />
```

```
      <atom id="a3" elementType="O" />
      <atom id="a4" elementType="H" />
      <atom id="a5" elementType="O" />
      <atom id="a6" elementType="H" />
      <atom id="a7" elementType="O" />
      <atom id="a8" elementType="H" />
    </atomArray>
    <bondArray>
      <bond atomRefs2="a1 a2" order="1" />
      <bond atomRefs2="a1 a5" order="1" />
      <bond atomRefs2="a1 a6" order="1" />
      <bond atomRefs2="a2 a4" order="1" />
      <bond atomRefs2="a2 a3" order="2" />
      <bond atomRefs2="a5 a7" order="1" />
      <bond atomRefs2="a7 a8" order="1" />
    </bondArray>
    <propertyList>
      <property dictRef="me:ZPE">
        <scalar units="kcal/mol">-22.3</scalar>
      </property>
      <property dictRef="me:rotConsts">
        <array units="cm-1">0.575612 0.099941 0.085156</array>
      </property>
      <property dictRef="me:symmetryNumber">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:frequenciesScaleFactor">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:vibFreqs">
        <array units="cm-1">3804 3233 3062 1574 1520 1412 1336 1235 1135 948 844 700 639
430 251 235 137 35</array>
      </property>
      <property dictRef="me:MW">
        <scalar units="amu">75</scalar>
      </property>
      <property dictRef="me:spinMultiplicity">
        <scalar>2</scalar>
      </property>
      <property dictRef="me:epsilon">
        <scalar>473.17</scalar>
      </property>
      <property dictRef="me:sigma">
        <scalar>5.09</scalar>
      </property>
    </propertyList>
```

```
    <me:energyTransferModel xsi:type="me:ExponentialDown">
      <me:deltaEDown units="cm-1">130</me:deltaEDown>
    </me:energyTransferModel>
    <me:DOSCMethod xsi:type="ClassicalRotors"/>
  </molecule>
        <molecule id="glyoxal">
    <atomArray>
      <atom id="a1" elementType="C" />
      <atom id="a2" elementType="C" />
      <atom id="a3" elementType="O" />
      <atom id="a4" elementType="O" />
      <atom id="a5" elementType="H" />
                <atom id="a6" elementType="H" />
    </atomArray>
    <bondArray>
      <bond atomRefs2="a1 a2" order="1" />
      <bond atomRefs2="a1 a5" order="1" />
      <bond atomRefs2="a1 a4" order="2" />
      <bond atomRefs2="a2 a6" order="1" />
      <bond atomRefs2="a2 a3" order="2" />
    </bondArray>
    <propertyList>
      <property dictRef="me:ZPE">
        <scalar units="kcal/mol">-47.5</scalar>
      </property>
      <property dictRef="me:rotConsts">
        <array units="cm-1">1.861549 0.159348 0.146783</array>
      </property>
      <property dictRef="me:symmetryNumber">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:frequenciesScaleFactor">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:vibFreqs">
        <array units="cm-1">2996 2991 1776 1753 1383 1342 1095 1066 818 560 332
130</array>
      </property>
      <property dictRef="me:MW">
        <scalar units="amu">58</scalar>
      </property>
      <property dictRef="me:spinMultiplicity">
        <scalar>2</scalar>
      </property>
      <property dictRef="me:epsilon">
        <scalar>473.17</scalar>
```

```
      </property>
      <property dictRef="me:sigma">
        <scalar>5.09</scalar>
      </property>
    </propertyList>
    <me:energyTransferModel xsi:type="me:ExponentialDown">
      <me:deltaEDown units="cm-1">130</me:deltaEDown>
    </me:energyTransferModel>
    <me:DOSCMethod xsi:type="ClassicalRotors"/>
  </molecule>
</moleculeList>
<reactionList>
  <reaction id="R1">
    <reactant>
      <molecule ref="vinoxy" role="deficientReactant" />
    </reactant>
    <reactant>
      <molecule ref="O2" role="excessReactant" />
    </reactant>
    <product>
      <molecule ref="PRa" role="modelled" />
    </product>
    <me:MCRCMethod xsi:type="me:MesmerILT">
      <me:preExponential units="cm3molecule-1s-1">1.04e-13</me:preExponential>
      <me:activationEnergy units="kcal/mol">0.4</me:activationEnergy>
      <me:TInfinity>298.0</me:TInfinity>
      <me:nInfinity>-0.5</me:nInfinity>
    </me:MCRCMethod>
    <me:excessReactantConc>4.90E18</me:excessReactantConc>
  </reaction>
        <reaction id="R2">
    <reactant>
      <molecule ref="PRa" role="modelled" />
    </reactant>
    <product>
      <molecule ref="QR1" role="modelled" />
    </product>
    <me:transitionState>
      <molecule ref="TS1" role="transitionState" />
    </me:transitionState>
    <me:tunneling name="Eckart"/>
    <me:MCRCMethod name="RRKM"/>
  </reaction>
        <reaction id="R3">
    <reactant>
      <molecule ref="PRa" role="modelled" />
```

```
  </reactant>
  <product>
    <molecule ref="glyoxal" role="sink" />
  </product>
        <product>
    <molecule ref="OH" role="sink" />
  </product>
  <me:transitionState>
    <molecule ref="TS2" role="transitionState" />
  </me:transitionState>
  <me:tunneling name="Eckart"/>
  <me:MCRCMethod name="RRKM"/>
</reaction>
      <reaction id="R4">
  <reactant>
    <molecule ref="QR1" role="modelled" />
  </reactant>
  <product>
    <molecule ref="H2CO" role="sink" />
  </product>
        <product>
    <molecule ref="CO" role="sink" />
  </product>
        <product>
    <molecule ref="OH" role="sink" />
  </product>
  <me:transitionState>
    <molecule ref="TS4" role="transitionState" />
  </me:transitionState>
  <me:MCRCMethod name="RRKM"/>
</reaction>
      <reaction id="R5">
  <reactant>
    <molecule ref="QR1" role="modelled" />
  </reactant>
  <product>
    <molecule ref="ketene" role="sink" />
  </product>
        <product>
    <molecule ref="HO2" role="sink" />
  </product>
  <me:transitionState>
    <molecule ref="TS5" role="transitionState" />
  </me:transitionState>
  <me:MCRCMethod name="RRKM"/>
</reaction>
```

```
  </reactionList>
  <me:conditions>
    <me:bathGas>N2</me:bathGas>
    <me:PTs>
      <me:PTpair units="Torr" P="760" T="298." />
      <!--<me:PTpair units="Torr" P="201.60" T="298." />-->
      <!--<me:PTpair units="Torr" P="10.06" T="298." />-->
      <!--<me:PTpair units="Torr" P="15.01" T="298." />-->

    </me:PTs>
  </me:conditions>
  <me:modelParameters>
    <!--Specify grain size directly...-->
    <me:grainSize units="cm-1">100</me:grainSize>
    <!--...or by the total number of grains
       <me:numberOfGrains> 500 </me:numberOfGrains>-->
    <!--Specify increased energy range
       <me:maxTemperature>6000</me:maxTemperature>-->
    <me:energyAboveTheTopHill>25.0</me:energyAboveTheTopHill>
  </me:modelParameters>
  <me:control>
    <me:testDOS />
    <me:printSpeciesProfile />
    <!--<me:testMicroRates />-->
    <me:testRateConstant />
    <me:printGrainDOS />
    <!--<me:printCellDOS />-->
    <!--<me:printReactionOperatorColumnSums />-->
    <!--<me:printTunnellingCoefficients />-->
    <me:printGrainkfE />
    <!--<me:printGrainBoltzmann />-->
    <me:printGrainkbE />
    <me:eigenvalues>0</me:eigenvalues>
    <!--<me:hideInactive/>-->
    <me:diagramEnergyOffset ref="R1">0</me:diagramEnergyOffset>
  </me:control>
</me:mesmer>
```

2-methyl-vinoxy + O_2 MESMER input

```
<?xml version="1.0" encoding="utf-8" ?>
<?xml-stylesheet type='text/xsl' href='../../mesmer2.xsl' media='other'?>
<?xml-stylesheet type='text/xsl' href='../../mesmer1.xsl' media='screen'?>
<me:mesmer xmlns="http://www.xml-cml.org/schema"
        xmlns:me="http://www.chem.leeds.ac.uk/mesmer"
        xmlns:xsi="http://www.w3.org/2001/XMLSchema-instance">
 <me:title> 2-methyl-vinoxy O2 Association</me:title>
 <moleculeList>
  <molecule id="MVR">
   <atomArray>
    <atom id="a1" elementType="C" />
    <atom id="a2" elementType="H" />
    <atom id="a3" elementType="H" />
    <atom id="a4" elementType="H" />
    <atom id="a5" elementType="C" />
    <atom id="a6" elementType="H" />
            <atom id="a7" elementType="C" />
    <atom id="a8" elementType="H" />
    <atom id="a9" elementType="O" />
   </atomArray>
   <bondArray>
    <bond atomRefs2="a1 a2" order="1" />
    <bond atomRefs2="a1 a3" order="1" />
    <bond atomRefs2="a1 a4" order="1" />
    <bond atomRefs2="a1 a5" order="1" />
    <bond atomRefs2="a5 a6" order="1" />
    <bond atomRefs2="a5 a7" order="1" />
    <bond atomRefs2="a7 a8" order="1" />
    <bond atomRefs2="a7 a9" order="2" />
   </bondArray>
   <propertyList>
    <property dictRef="me:ZPE">
     <scalar units="kcal/mol">0.0</scalar>
    </property>
    <property dictRef="me:rotConsts">
     <array units="cm-1">0.6583 0.19553 0.155021</array>
    </property>
    <property dictRef="me:symmetryNumber">
     <scalar>1</scalar>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
     <scalar>1</scalar>
    </property>
    <property dictRef="me:vibFreqs">
```

```
        <array units="cm-1">102.7 273.4 300.2 640.2 700.3 890.9 957.9 1022.7 1068.9 1180.6
1396.8 1418.8 1431.5 1488.9 1500.4 1644.1 2964.9 3032.0 3074.7 3158.1 3194 </array>
       </property>
       <property dictRef="me:MW">
        <scalar units="amu">57</scalar>
       </property>
       <property dictRef="me:spinMultiplicity">
        <scalar>2</scalar>
       </property>
      </propertyList>
      <me:DOSCMethod xsi:type="ClassicalRotors"/>
     </molecule>
     <molecule id="O2" description="oxygen">
      <atomArray>
       <atom id="a1" elementType="O" />
       <atom id="a2" elementType="O" />
      </atomArray>
      <bondArray>
       <bond atomRefs2="a1 a2" order="2" />
      </bondArray>
      <propertyList>
       <property dictRef="me:ZPE">
        <scalar units="kcal/mol">0.0</scalar>
       </property>
       <property dictRef="me:rotConsts">
        <array units="cm-1">1.431782</array>
       </property>
       <property dictRef="me:symmetryNumber">
        <scalar>2</scalar>
       </property>
       <property dictRef="me:frequenciesScaleFactor">
        <scalar>1</scalar>
       </property>
       <property dictRef="me:vibFreqs">
        <array units="cm-1">1583</array>
       </property>
       <property dictRef="me:MW">
        <scalar units="amu">32</scalar>
       </property>
       <property dictRef="me:spinMultiplicity">
        <scalar>3</scalar>
       </property>
      </propertyList>
      <me:DOSCMethod xsi:type="ClassicalRotors"/>
     </molecule>
     <molecule id="OH" description="OH radical">
```

```
  <atomArray>
    <atom id="a1" elementType="O" />
    <atom id="a2" elementType="H" />
  </atomArray>
  <bondArray>
    <bond atomRefs2="a1 a2" order="1" />
  </bondArray>
  <propertyList>
    <property dictRef="me:ZPE">
      <scalar units="kcal/mol">0.0</scalar>
    </property>
    <property dictRef="me:rotConsts">
      <array units="cm-1">18.86743</array>
    </property>
    <property dictRef="me:symmetryNumber">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:vibFreqs">
      <array units="cm-1">3718</array>
    </property>
    <property dictRef="me:MW">
      <scalar units="amu">17</scalar>
    </property>
    <property dictRef="me:spinMultiplicity">
      <scalar>2</scalar>
    </property>
    <property dictRef="me:eletronicExcitation">
      <array units="cm-1">139.7</array>
    </property>
  </propertyList>
  <me:DOSCMethod xsi:type="ClassicalRotors"/>
</molecule>
<molecule id="PRa" description="peroxy vinoxy O2 adduct">
  <atomArray>
    <atom id="a1" elementType="C" />
    <atom id="a2" elementType="C" />
    <atom id="a3" elementType="O" />
    <atom id="a4" elementType="H" />
    <atom id="a5" elementType="O" />
    <atom id="a6" elementType="O" />
    <atom id="a7" elementType="H" />
    <atom id="a8" elementType="C" />
    <atom id="a9" elementType="H" />
```

```
      <atom id="a10" elementType="H" />
      <atom id="a11" elementType="H" />
    </atomArray>
    <bondArray>
      <bond atomRefs2="a1 a2" order="1" />
      <bond atomRefs2="a1 a7" order="1" />
      <bond atomRefs2="a1 a8" order="1" />
      <bond atomRefs2="a1 a5" order="1" />
      <bond atomRefs2="a2 a3" order="2" />
      <bond atomRefs2="a2 a4" order="1" />
      <bond atomRefs2="a8 a9" order="1" />
      <bond atomRefs2="a8 a10" order="1" />
      <bond atomRefs2="a8 a11" order="1" />
      <bond atomRefs2="a5 a6" order="1" />
    </bondArray>
    <propertyList>
      <property dictRef="me:ZPE">
        <scalar units="kcal/mol">-21.5</scalar>
      </property>
      <property dictRef="me:rotConsts">
        <array units="cm-1">0.186276354 0.093111055 0.065640364</array>
      </property>
      <property dictRef="me:symmetryNumber">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:frequenciesScaleFactor">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:vibFreqs">
        <array units="cm-1">47.9 131.2 207.6 242.3 283.8 414.1 472.2 604 835.4 895.4 928.5
1082.8 1094.0 1127.4 1182.3 1313 1335.8 1400 1417.1 1493.3 1503.6 1781.8 2990.5 3067.2
3087 3160 3171.8</array>
      </property>
      <property dictRef="me:MW">
        <scalar units="amu">89</scalar>
      </property>
      <property dictRef="me:spinMultiplicity">
        <scalar>2</scalar>
      </property>
      <property dictRef="me:epsilon">
        <scalar>473.17</scalar>
      </property>
      <property dictRef="me:sigma">
        <scalar>5.09</scalar>
      </property>
    </propertyList>
```

```
  <me:energyTransferModel xsi:type="me:ExponentialDown">
    <me:deltaEDown units="cm-1">130</me:deltaEDown>
  </me:energyTransferModel>
  <me:DOSCMethod xsi:type="ClassicalRotors"/>
</molecule>
<molecule id="TS1" description="TS1a: PRa -> QR1">
  <atomArray>
    <atom id="a1" elementType="C" />
    <atom id="a2" elementType="C" />
    <atom id="a3" elementType="O" />
    <atom id="a4" elementType="H" />
    <atom id="a5" elementType="O" />
    <atom id="a6" elementType="O" />
    <atom id="a7" elementType="C" />
    <atom id="a8" elementType="H" />
    <atom id="a9" elementType="H" />
    <atom id="a10" elementType="H" />
    <atom id="a11" elementType="H" />
  </atomArray>
  <bondArray>
    <bond atomRefs2="a1 a2" order="1" />
    <bond atomRefs2="a1 a8" order="1" />
    <bond atomRefs2="a1 a7" order="1" />
    <bond atomRefs2="a1 a5" order="1" />
    <bond atomRefs2="a5 a6" order="1" />
                <bond atomRefs2="a7 a9" order="1" />
                <bond atomRefs2="a7 a10" order="1" />
                <bond atomRefs2="a7 a11" order="1" />
                <bond atomRefs2="a2 a4" order="1" />
                <bond atomRefs2="a2 a3" order="2" />
  </bondArray>
  <propertyList>
    <property dictRef="me:ZPE">
      <scalar units="kcal/mol">-1.1</scalar>
    </property>
    <property dictRef="me:rotConsts">
      <array units="cm-1">0.153311532 0.115148817 0.069511665</array>
    </property>
    <property dictRef="me:symmetryNumber">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:vibFreqs">
```

<array units="cm-1">149.7 204.4 233.3 288 414.3 506.6575.1136 674.8190 751.7762
870.3413 921.8204 990.4815 1103.1380 1132.0032 1179.6469 1272.4483 1333.7250 1414.0624
1488.1788 1501.2280 1828.7960 1911.8811 3048.9239 3064.8311 3158.5322 3162.7378
</array>
</property>
<property dictRef="me:MW">
<scalar units="amu">89</scalar>
</property>
<property dictRef="me:spinMultiplicity">
<scalar>2</scalar>
</property>
<property dictRef="me:imFreqs">
<scalar units="cm-1">2171.7</scalar>
</property>
</propertyList>
<me:DOSCMethod xsi:type="ClassicalRotors"/>
</molecule>
<molecule id="QR1">
<atomArray>
<atom id="a1" elementType="O" />
<atom id="a2" elementType="C" />
<atom id="a3" elementType="C" />
<atom id="a4" elementType="O" />
<atom id="a5" elementType="O" />
<atom id="a6" elementType="H" />
<atom id="a7" elementType="H" />
<atom id="a8" elementType="C" />
<atom id="a9" elementType="H" />
<atom id="a10" elementType="H" />
<atom id="a11" elementType="H" />
</atomArray>
<bondArray>
<bond atomRefs2="a2 a1" order="2" />
<bond atomRefs2="a2 a3" order="1" />
<bond atomRefs2="a3 a8" order="1" />
<bond atomRefs2="a3 a7" order="1" />
<bond atomRefs2="a3 a4" order="1" />
<bond atomRefs2="a8 a9" order="1" />
<bond atomRefs2="a8 a10" order="1" />
<bond atomRefs2="a8 a11" order="1" />
<bond atomRefs2="a4 a5" order="1" />
<bond atomRefs2="a5 a6" order="1" />
</bondArray>
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kcal/mol">-20</scalar>

```
    </property>
    <property dictRef="me:rotConsts">
      <array units="cm-1">0.144487634 0.122939961 0.072846032 </array>
    </property>
    <property dictRef="me:symmetryNumber">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:vibFreqs">
      <array units="cm-1">119.4818 161.8741 214.1119 244.0278
        311.5554 362.6836 409.2454 512.638 668.0661 738.5844
        837.2351 919.8197 1028.7648 1113.4922 1165.3845 1298.2956
        1333.3916 1382.1359 1408.6773 1490.0535 1506.6147 1873.1
        3065.7637 3070.3675 3158.9006 3168.7117 3734.9548 </array>
    </property>
    <property dictRef="me:MW">
      <scalar units="amu">89</scalar>
    </property>
    <property dictRef="me:spinMultiplicity">
      <scalar>2</scalar>
    </property>
    <property dictRef="me:epsilon">
      <scalar>473.17</scalar>
    </property>
    <property dictRef="me:sigma">
      <scalar>5.09</scalar>
    </property>
  </propertyList>
  <me:energyTransferModel xsi:type="me:ExponentialDown">
    <me:deltaEDown units="cm-1">130</me:deltaEDown>
  </me:energyTransferModel>
  <me:DOSCMethod xsi:type="ClassicalRotors"/>
</molecule>
<molecule id="TS7" description="QR1 -> AA + OH">
  <atomArray>
    <atom id="a1" elementType="C" />
    <atom id="a2" elementType="C" />
    <atom id="a3" elementType="O" />
    <atom id="a4" elementType="H" />
    <atom id="a5" elementType="C" />
    <atom id="a6" elementType="O" />
    <atom id="a7" elementType="H" />
    <atom id="a8" elementType="O" />
    <atom id="a9" elementType="H" />
```

```
      <atom id="a10" elementType="H" />
      <atom id="a11" elementType="H" />
    </atomArray>
    <bondArray>
      <bond atomRefs2="a1 a4" order="1" />
      <bond atomRefs2="a1 a5" order="1" />
      <bond atomRefs2="a1 a3" order="1" />
      <bond atomRefs2="a3 a6" order="1" />
      <bond atomRefs2="a6 a7" order="1" />
                <bond atomRefs2="a5 a9" order="1" />
                <bond atomRefs2="a5 a10" order="1" />
                <bond atomRefs2="a5 a11" order="1" />
                <bond atomRefs2="a2 a8" order="2" />
                <bond atomRefs2="a1 a2" order="1" />
    </bondArray>
    <propertyList>
      <property dictRef="me:ZPE">
        <scalar units="kcal/mol">-10.4</scalar>
      </property>
      <property dictRef="me:rotConsts">
        <array units="cm-1">0.131349695      0.111125411   0.065286949</array>
      </property>
      <property dictRef="me:symmetryNumber">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:frequenciesScaleFactor">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:vibFreqs">
        <array units="cm-1">84.0362 140.1260 179.6395 186.4707 241.3967 298.7336 363.9915
390.7807 498.1598 826.3831 867.8235 946.4621 1080.3370 1138.6187 1196.3859 1343.2065
1382.0938 1411.8039 1480.8700 1497.9828 1926.6867 3045.9431 3128.3977 3152.6257
3162.3120 3735.6955 </array>
      </property>
      <property dictRef="me:MW">
        <scalar units="amu">89</scalar>
      </property>
      <property dictRef="me:spinMultiplicity">
        <scalar>2</scalar>
      </property>
      <property dictRef="me:imFreqs">
        <scalar units="cm-1">374.7</scalar>
      </property>
    </propertyList>
    <me:DOSCMethod xsi:type="ClassicalRotors"/>
  </molecule>
```

```
   <molecule id="AA" description="acetaldehyde">
     <atomArray>
       <atom id="a1" elementType="O" />
       <atom id="a2" elementType="C" />
       <atom id="a3" elementType="H" />
       <atom id="a4" elementType="C" />
       <atom id="a5" elementType="H" />
       <atom id="a6" elementType="H" />
       <atom id="a7" elementType="H" />
     </atomArray>
     <bondArray>
       <bond atomRefs2="a1 a2" order="2" />
       <bond atomRefs2="a2 a3" order="1" />
       <bond atomRefs2="a2 a4" order="1" />
       <bond atomRefs2="a4 a5" order="1" />
       <bond atomRefs2="a4 a6" order="1" />
       <bond atomRefs2="a4 a7" order="1" />
     </bondArray>
     <propertyList>
       <property dictRef="me:ZPE">
         <scalar units="kcal/mol">-51.4</scalar>
       </property>
       <property dictRef="me:rotConsts">
         <array units="cm-1">1.88351209289 0.33339240642 0.29910086664</array>
       </property>
       <property dictRef="me:symmetryNumber">
         <scalar>1</scalar>
       </property>
       <property dictRef="me:frequenciesScaleFactor">
         <scalar>1</scalar>
       </property>
       <property dictRef="me:vibFreqs">
         <array units="cm-1">161.7390 500.1649 777.9218 893.4781 1133.4279 1133.9569
1386.6734 1436.2800 1470.5689 1480.9939 1788.1627 2942.3685 3046.0761 3124.4385
3173.3554 </array>
       </property>
       <property dictRef="me:MW">
         <scalar units="amu">44</scalar>
       </property>
       <property dictRef="me:spinMultiplicity">
         <scalar>1</scalar>
       </property>
     </propertyList>
     <me:DOSCMethod xsi:type="ClassicalRotors"/>
   </molecule>
   <molecule id="HO2">
```

```
  <atomArray>
    <atom id="a1" elementType="O" />
    <atom id="a2" elementType="H" />
    <atom id="a3" elementType="O" />
  </atomArray>
  <bondArray>
    <bond atomRefs2="a1 a2" order="1" />
    <bond atomRefs2="a1 a3" order="1" />
  </bondArray>
  <propertyList>
    <property dictRef="me:ZPE">
      <scalar units="kcal/mol">0.0</scalar>
    </property>
    <property dictRef="me:rotConsts">
      <array units="cm-1">20.52618 1.113085 1.05583</array>
    </property>
    <property dictRef="me:symmetryNumber">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:vibFreqs">
      <array units="cm-1">3674 1434 1126</array>
    </property>
    <property dictRef="me:MW">
      <scalar units="amu">33</scalar>
    </property>
    <property dictRef="me:spinMultiplicity">
      <scalar>2</scalar>
    </property>
  </propertyList>
  <me:DOSCMethod xsi:type="ClassicalRotors"/>
</molecule>
<molecule id="TS6" description="TS QR1 -> acrolein + HO2">
  <atomArray>
    <atom id="a1" elementType="O" />
    <atom id="a2" elementType="O" />
    <atom id="a3" elementType="H" />
    <atom id="a4" elementType="C" />
    <atom id="a5" elementType="C" />
    <atom id="a6" elementType="H" />
    <atom id="a7" elementType="C" />
    <atom id="a8" elementType="O" />
    <atom id="a9" elementType="H" />
    <atom id="a10" elementType="H" />
```

```
      <atom id="a11" elementType="H" />
    </atomArray>
    <bondArray>
      <bond atomRefs2="a1 a2" order="1" />
      <bond atomRefs2="a2 a3" order="1" />
      <bond atomRefs2="a1 a4" order="1" />
      <bond atomRefs2="a4 a6" order="1" />
      <bond atomRefs2="a4 a7" order="1" />
                <bond atomRefs2="a4 a5" order="1" />
                <bond atomRefs2="a7 a8" order="2" />
                <bond atomRefs2="a5 a9" order="1" />
                <bond atomRefs2="a5 a10" order="1" />
                <bond atomRefs2="a5 a11" order="1" />
    </bondArray>
    <propertyList>
      <property dictRef="me:ZPE">
        <scalar units="kcal/mol">5.4</scalar>
      </property>
      <property dictRef="me:rotConsts">
        <array units="cm-1">0.124845956 0.10580067 0.061647135 </array>
      </property>
      <property dictRef="me:symmetryNumber">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:frequenciesScaleFactor">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:vibFreqs">
        <array units="cm-1">66.0134 111.0556 166.4861 208.0358 215.7226 294.3885 417.8073
454.8312 587.6209 809.1091 853.0451 878.2032 1052.7450 1093.7971 1130.0228 1348.9879
1358.4240 1413.2528 1490.8083 1506.9533 2089.6717 3060.2337 3148.8575 3157.1418
3189.8719 3750.0007</array>
      </property>
      <property dictRef="me:MW">
        <scalar units="amu">89</scalar>
      </property>
      <property dictRef="me:spinMultiplicity">
        <scalar>2</scalar>
      </property>
      <property dictRef="me:imFreqs">
        <scalar units="cm-1">679.2</scalar>
      </property>
    </propertyList>
    <me:DOSCMethod xsi:type="ClassicalRotors"/>
  </molecule>
        <molecule id="TS5" description="TS PRa -> Acrolein + HO2">
```

```
    <atomArray>
      <atom id="a1" elementType="C" />
      <atom id="a2" elementType="C" />
      <atom id="a3" elementType="O" />
      <atom id="a4" elementType="C" />
      <atom id="a5" elementType="H" />
      <atom id="a6" elementType="H" />
      <atom id="a7" elementType="O" />
      <atom id="a8" elementType="O" />
      <atom id="a9" elementType="H" />
      <atom id="a10" elementType="H" />
      <atom id="a11" elementType="H" />
    </atomArray>
    <bondArray>
      <bond atomRefs2="a1 a5" order="1" />
      <bond atomRefs2="a1 a4" order="1" />
      <bond atomRefs2="a1 a2" order="1" />
      <bond atomRefs2="a4 a8" order="2" />
      <bond atomRefs2="a4 a9" order="1" />
                <bond atomRefs2="a2 a10" order="1" />
                <bond atomRefs2="a2 a11" order="1" />
                <bond atomRefs2="a2 a6" order="1" />
                <bond atomRefs2="a3 a7" order="1" />
                <bond atomRefs2="a6 a7" order="1" />
    </bondArray>
    <propertyList>
      <property dictRef="me:ZPE">
        <scalar units="kcal/mol">5.8</scalar>
      </property>
      <property dictRef="me:rotConsts">
        <array units="cm-1">0.194135891 0.07945373 0.061507885 </array>
      </property>
      <property dictRef="me:symmetryNumber">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:frequenciesScaleFactor">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:vibFreqs">
        <array units="cm-1">101.1623 157.3840 198.2507 318.2747 336.2958 473.4515
563.2339 622.7663 652.7914 909.4821 967.1819 1009.6004 1038.2238 1169.4608 1249.9925
1282.0777 1298.4870 1387.5471 1448.0545 1557.2887 1588.3220 1760.2668 2955.4948
3126.4395 3212.6642 3228.5359</array>
      </property>
      <property dictRef="me:MW">
        <scalar units="amu">89</scalar>
```

```
    </property>
    <property dictRef="me:spinMultiplicity">
      <scalar>2</scalar>
    </property>
    <property dictRef="me:imFreqs">
      <scalar units="cm-1">1469.1</scalar>
    </property>
  </propertyList>
  <me:DOSCMethod xsi:type="ClassicalRotors"/>
</molecule>
<molecule id="MK" description="methylketene">
  <atomArray>
    <atom id="a1" elementType="C" />
    <atom id="a2" elementType="H" />
    <atom id="a3" elementType="C" />
    <atom id="a4" elementType="H" />
    <atom id="a5" elementType="H" />
    <atom id="a6" elementType="H" />
    <atom id="a7" elementType="C" />
    <atom id="a8" elementType="O" />
  </atomArray>
  <bondArray>
    <bond atomRefs2="a1 a2" order="1" />
    <bond atomRefs2="a1 a3" order="1" />
    <bond atomRefs2="a3 a4" order="1" />
    <bond atomRefs2="a3 a5" order="1" />
    <bond atomRefs2="a3 a6" order="1" />
    <bond atomRefs2="a1 a7" order="2" />
    <bond atomRefs2="a7 a8" order="2" />
  </bondArray>
  <propertyList>
    <property dictRef="me:ZPE">
      <scalar units="kcal/mol">-5.4</scalar>
    </property>
    <property dictRef="me:rotConsts">
      <array units="cm-1">1.27385261640 0.14765183986 0.13571183635</array>
    </property>
    <property dictRef="me:symmetryNumber">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
      <scalar>1</scalar>
    </property>
    <property dictRef="me:vibFreqs">
```

```
        <array units="cm-1">147.2285 210.9291 506.3963 516.6623 636.0791 899.6395
1058.8120 1086.0117 1146.0031 1403.4186 1426.0287 1491.2166 1518.9981 2183.5531
3047.8424 3122.7514 3142.6408 3223.7096</array>
       </property>
       <property dictRef="me:MW">
        <scalar units="amu">56</scalar>
       </property>
       <property dictRef="me:spinMultiplicity">
        <scalar>1</scalar>
       </property>
      </propertyList>
      <me:energyTransferModel xsi:type="me:ExponentialDown">
       <me:deltaEDown units="cm-1">130</me:deltaEDown>
      </me:energyTransferModel>
      <me:DOSCMethod xsi:type="ClassicalRotors"/>
     </molecule>
          <molecule id="AC" description="acrolein">
      <atomArray>
       <atom id="a1" elementType="C" />
       <atom id="a2" elementType="C" />
       <atom id="a3" elementType="O" />
       <atom id="a4" elementType="H" />
       <atom id="a5" elementType="C" />
       <atom id="a6" elementType="H" />
       <atom id="a7" elementType="H" />
       <atom id="a8" elementType="H" />
      </atomArray>
      <bondArray>
       <bond atomRefs2="a1 a2" order="1" />
       <bond atomRefs2="a2 a3" order="2" />
       <bond atomRefs2="a2 a4" order="1" />
       <bond atomRefs2="a1 a5" order="2" />
       <bond atomRefs2="a1 a6" order="1" />
       <bond atomRefs2="a5 a7" order="1" />
       <bond atomRefs2="a5 a8" order="1" />
      </bondArray>
      <propertyList>
       <property dictRef="me:ZPE">
        <scalar units="kcal/mol">-5.8</scalar>
       </property>
       <property dictRef="me:rotConsts">
        <array units="cm-1">0.75150219423 0.20481030247 0.16094675404</array>
       </property>
       <property dictRef="me:symmetryNumber">
        <scalar>1</scalar>
       </property>
```

```
      <property dictRef="me:frequenciesScaleFactor">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:vibFreqs">
        <array units="cm-1">146.8007 277.0260 548.9944 672.5681 930.6977 966.6829
1004.0936 1020.6778 1059.8673 1300.7811 1428.5506 1438.2732 1655.5894 1753.9522
2964.9658 3164.4652 3193.2212 3269.9215</array>
      </property>
      <property dictRef="me:MW">
        <scalar units="amu">56</scalar>
      </property>
      <property dictRef="me:spinMultiplicity">
        <scalar>1</scalar>
      </property>
    </propertyList>
    <me:energyTransferModel xsi:type="me:ExponentialDown">
      <me:deltaEDown units="cm-1">130</me:deltaEDown>
    </me:energyTransferModel>
    <me:DOSCMethod xsi:type="ClassicalRotors"/>
  </molecule>
       <molecule id="CO">
    <atomArray>
      <atom id="a1" elementType="C" />
      <atom id="a2" elementType="O" />
    </atomArray>
    <bondArray>
      <bond atomRefs2="a1 a2" order="2" />
    </bondArray>
    <propertyList>
      <property dictRef="me:ZPE">
        <scalar units="kcal/mol">0</scalar>
      </property>
      <property dictRef="me:rotConsts">
        <array units="cm-1">1.905061</array>
      </property>
      <property dictRef="me:symmetryNumber">
        <scalar>2</scalar>
      </property>
      <property dictRef="me:frequenciesScaleFactor">
        <scalar>1</scalar>
      </property>
      <property dictRef="me:vibFreqs">
        <array units="cm-1">2146</array>
      </property>
      <property dictRef="me:MW">
        <scalar units="amu">28</scalar>
```

```
      </property>
      <property dictRef="me:spinMultiplicity">
        <scalar>1</scalar>
      </property>
    </propertyList>
    <me:DOSCMethod xsi:type="ClassicalRotors"/>
  </molecule>
</moleculeList>
<reactionList>
  <reaction id="R1">
    <reactant>
      <molecule ref="MVR" role="deficientReactant" />
    </reactant>
    <reactant>
      <molecule ref="O2" role="excessReactant" />
    </reactant>
    <product>
      <molecule ref="PRa" role="modelled" />
    </product>
    <me:MCRCMethod xsi:type="me:MesmerILT">
      <me:preExponential units="cm3molecule-1s-1">1.3e-12</me:preExponential>
      <me:activationEnergy units="kcal/mol">0.4</me:activationEnergy>
      <me:TInfinity>298.0</me:TInfinity>
      <me:nInfinity>-0.5</me:nInfinity>
    </me:MCRCMethod>
    <me:excessReactantConc>4.9E18</me:excessReactantConc>
  </reaction>
        <reaction id="R2">
    <reactant>
      <molecule ref="PRa" role="modelled" />
    </reactant>
    <product>
      <molecule ref="QR1" role="modelled" />
    </product>
    <me:transitionState>
      <molecule ref="TS1" role="transitionState" />
    </me:transitionState>
    <me:tunneling name="Eckart"/>
    <me:MCRCMethod name="RRKM"/>
  </reaction>
        <reaction id="R3">
    <reactant>
      <molecule ref="PRa" role="modelled" />
    </reactant>
    <product>
      <molecule ref="AC" role="sink" />
```

```
    </product>
          <product>
      <molecule ref="HO2" role="sink" />
    </product>
    <me:transitionState>
      <molecule ref="TS5" role="transitionState" />
    </me:transitionState>
    <me:MCRCMethod name="RRKM"/>
  </reaction>
        <reaction id="R4">
    <reactant>
      <molecule ref="QR1" role="modelled" />
    </reactant>
    <product>
      <molecule ref="AA" role="sink" />
    </product>
          <product>
      <molecule ref="CO" role="sink" />
    </product>
          <product>
      <molecule ref="OH" role="sink" />
    </product>
    <me:transitionState>
      <molecule ref="TS7" role="transitionState" />
    </me:transitionState>
    <me:MCRCMethod name="RRKM"/>
  </reaction>
        <reaction id="R5">
    <reactant>
      <molecule ref="QR1" role="modelled" />
    </reactant>
    <product>
      <molecule ref="MK" role="sink" />
    </product>
          <product>
      <molecule ref="HO2" role="sink" />
    </product>
    <me:transitionState>
      <molecule ref="TS6" role="transitionState" />
    </me:transitionState>
    <me:MCRCMethod name="RRKM"/>
  </reaction>
</reactionList>
<me:conditions>
  <me:bathGas>N2</me:bathGas>
  <me:PTs>
```

```
      <me:PTpair units="Torr" P="760" T="298." />
      <!--<me:PTpair units="Torr" P="201.60" T="298." />-->
      <!--<me:PTpair units="Torr" P="10.06" T="298." />-->
      <!--<me:PTpair units="Torr" P="15.01" T="298." />-->
    </me:PTs>
  </me:conditions>
  <me:modelParameters>
    <!--Specify grain size directly...-->
    <me:grainSize units="cm-1">100</me:grainSize>
    <!--...or by the total number of grains
       <me:numberOfGrains> 500 </me:numberOfGrains>-->
    <!--Specify increased energy range
       <me:maxTemperature>6000</me:maxTemperature>-->
    <me:energyAboveTheTopHill>25.0</me:energyAboveTheTopHill>
  </me:modelParameters>
  <me:control>
    <me:testDOS />
    <me:printSpeciesProfile />
    <!--<me:testMicroRates />-->
    <me:testRateConstant />
    <me:printGrainDOS />
    <!--<me:printCellDOS />-->
    <!--<me:printReactionOperatorColumnSums />-->
    <!--<me:printTunnellingCoefficients />-->
    <me:printGrainkfE />
    <!--<me:printGrainBoltzmann />-->
    <me:printGrainkbE />
    <me:eigenvalues>0</me:eigenvalues>
    <!--<me:hideInactive/>-->
    <me:diagramEnergyOffset ref="R1">0</me:diagramEnergyOffset>
  </me:control>
</me:mesmer>
```

References

1. Kuwata, K. T.; Valin, L. C. Quantum Chemical and RRKM/Master Equation Studies of Isoprene Ozonolysis: Methacrolein and Methacrolein Oxide. *Chem. Phys. Lett.* **2008,** *451*, 186-191.
2. Carr, S. A.; Glowacki, D. R.; Liang, C.-H.; Baeza-Romero, M. T.; Blitz, M. A.; Pilling, M. J.; Seakins, P. W. Experimental and Modeling Studies of the Pressure and Temperature Dependences of the Kinetics and the OH Yields in the Acetyl + O_2 Reaction. *J. Phys. Chem A* **2011,** *115*, 1069-1085.
3. Dodson, L. G.; Shen, L.; Savee, J. D.; Eddingsas, N. C.; Welz, O.; Taatjes, C. A.; Osborn, D. L.; Sander, S. P.; Okumura, M. VUV Photoionization Cross Sections of HO_2, H_2O_2, and H_2CO. *J. Phys. Chem. A* **2015,** *119*, 1279-1291.
4. Goulay, F.; Derakhshan, A.; Maher, E.; Trevitt, A. J.; Savee, J. D.; Scheer, A. M.; Osborn, D. L.; Taatjes, C. A. Formation of dimethylketene and methacrolein by reaction of the CH radical with acetone. *Phys. Chem. Chem. Phys.* **2013,** *15*, 4049-4058.
5. Egolfopoulos, F. N.; Hansen, N.; Ju, Y.; Kohse-Höinghaus, K.; Law, C. K.; Qi, F. Advances and challenges in laminar flame experiments and implications for combustion chemistry. *Prog. Energy Combust. Sci.* **2014,** *43*, 36-67.
6. Welz, O.; Zádor, J.; Savee, J. D.; Ng, M. Y.; Meloni, G.; Fernandez, R. X.; Sheps, L.; Simmons, B. A.; Lee, T. S.; Osborn, D. L., et al. Low-temperature combustion chemistry of biofuels: pathways in the initial low-temperature (550 K–750 K) oxidation chemistry of isopentanol. *Phys. Chem. Chem. Phys.* **2012,** *14*, 3112-3127.
7. Traeger, J. C.; McLoughlin, R. G.; Nicholson, A. J. C. Heat of formation for acetyl cation in the gas phase. *J. Am. Chem. Soc.* **1982,** *104*, 5318-5322.
8. Holmes, J. L.; Burgers, P. C.; Mollah, Y. A. Alkane elimination from ionized alkanols. *Org. Mass Spectrom.* **1982,** *17*, 127-130.
9. Bobeldijk, M.; Van der Zande, W. J.; Kistemaker, P. G. Simple models for the calculation of photoionization and electron impact ionization cross sections of polyatomic molecules. *Chem. Phys.* **1993,** *179*, 125-130.
10. Person, J. C.; Nicole, P. P. Isotope Effects in the Photoionization Yields and the Asborption Cross Sections for Ethylene and n-Butane. *J. Chem. Phys.* **1968,** *49*, 5421.
11. Weidman, J. D.; Allen, R. T.; MooreIII, K. B.; SchaeferIII, H. F. High-level theoretical characterization of the vinoxy radical (•CH_2CHO) + O_2 reaction. *J. Chem. Phys.* **2018,** *148*, 184308.
12. Davis, M. M.; Weidman, J. D.; Abbott, A. S.; Douberly, G. E.; Turney, J. M.; SchaeferIII, H. F. Characterization of the 2-methylvinoxy radical + O_2 reaction: A focal point analysis and composite multireference study. *J. Chem. Phys.* **2019,** *151*, 124302.