The Mechanism of the Reaction of OH with Alkynes in the Presence of Oxygen

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Supplementary Information

I. Rate Coefficient Data for OH + alkynes in nitrogen

OH + Propyne

Temperature/K	Pressure/Torr	10^{12} × Rate Coefficient/cm^3 molecule^{-1} s^{-1}
212	5	2.53 ± 0.25[a]
212	10	3.17 ± 0.32
212	20	3.05 ± 0.31
295[b]	5	2.65 ± 0.27
295[c]	5	2.73 ± 0.27
388	5	3.14 ± 0.31
388	5	3.27 ± 0.33
388	5	3.15 ± 0.32
498	5	2.39 ± 0.24
498	5	2.53 ± 0.25
498	5	2.37 ± 0.24
498	5	2.39 ± 0.24

OH + But-2-yne

Temperature/K	Pressure/Torr	10^{11} × Rate Coefficient/cm^3 molecule^{-1} s^{-1}
212	10	2.58 ± 0.26
212	20	3.04 ± 0.30
295[b]	10	1.66 ± 0.17
295[c]	10	1.80 ± 0.18
388	10	1.42 ± 0.14
498	10	1.11 ± 0.14
498	20	1.40 ± 0.14
498	30	1.51 ± 0.15

a – Errors are a combination of statistical from the bimolecular plot and estimates of systematic errors.

b – Room temperature data measured in the low temperature cell.

c – Room temperature data measured in the high temperature cell.

II. Mesmer Input file

Further information on the layout of the programmes can be found in the MESMER manual, available from http://sourceforge.net/projects/mesmer/.

```
<me:mesmer xmlns="http://www.xml-cml.org/schema"
xmlns:me="http://www.chem.leeds.ac.uk/mesmer">
  <title> Acetyl O2 association</title>
<!--Data from Carr et al, J. Phys. Chem. A 2011, 115, 1069 1085-->
<moleculeList>
    <molecule id="acetyl" description="CH_3CO">
      <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="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="2"/>
      </bondArray>
      <propertyList>
        <property dictRef="me:ZPE">
          <scalar units="kJ/mol">0</scalar>
        </property>
        <property dictRef="me:rotConsts">
          <array units="cm-1">1.573140 0.3155 0.3330</array>
        </property>
        <property dictRef="me:symmetryNumber">
          <scalar>3</scalar>
        </property>
        <property dictRef="me:frequenciesScaleFactor">
          <scalar>0.9854</scalar>
        </property>
        <property dictRef="me:vibFreqs">
          <array units="cm-1">110.8594 469.8360 852.9605 955.5673 1049.6839
1359.1474 1454.3118 1459.6421 1930.1084 3014.0596 3104.5876 3110.7727 </array>
        </property>
        <property dictRef="me:MW">
          <scalar units="amu">43</scalar>
        </property>
        <property dictRef="me:spinMultiplicity">
          <scalar>2</scalar>
        </property>
           <property dictRef="me:epsilon">
          <scalar>500</scalar>
        </property>
        <property dictRef="me:sigma">
          <scalar>3.09</scalar>
        </property>
        <property dictRef="me:deltaEDown">
          <scalar units="cm-1">200.0</scalar>
        </property>
      </propertyList>
      <me:DOSCMethod>Classical rotors</me:DOSCMethod>
```

```
 <me:DistributionCalcMethod CoFragment="AceticAcid" EnergyExcess="585"
units="kJ/mol">Prior </me:DistributionCalcMethod>
    </molecule>


        <molecule id="TSdecomp">
      <propertyList>
   <!-- Data from Lee,Int. J. Chem. Kinet. 2003, 35, 20-44 -->
        <property dictRef="me:ZPE">
          <scalar units="kJ/mol">72</scalar>
        </property>
        <property dictRef="me:rotConsts">
          <array units="cm-1">2.15 0.271 0.253</array>
        </property>
        <property dictRef="me:symmetryNumber">
          <scalar>3</scalar>
        </property>
        <property dictRef="me:frequenciesScaleFactor">
          <scalar>0.90</scalar>
        </property>
        <property dictRef="me:vibFreqs">
          <!-- From  Huynh,  J. Org. Chem. 2008,73, 94-101 -->
          <array units="cm-1">51 338 662 756 1123 1537 1547 2209 3210 3352 3371
</array>
        </property>
        <property dictRef="me:MW">
          <scalar units="amu">43</scalar>
        </property>
        <property dictRef="me:imFreqs">
          <array units="cm-1">533.0</array>
        </property>
      </propertyList>
      <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
    </molecule>

    <molecule id="CO" description="oxygen">
      <propertyList>
        <property dictRef="me:ZPE">
          <scalar units="kJ/mol">177.44888</scalar>
        </property>
      </propertyList>
    </molecule>

        <molecule id="CH3" description="oxygen">
      <propertyList>
        <property dictRef="me:ZPE">
          <scalar units="kJ/mol">0.0</scalar>
        </property>
      </propertyList>
    </molecule>

<molecule id="AceticAcid">
     <propertyList>
       <property dictRef="me:rotConsts">
       <!-- Taken from http://cccbdb.nist.gov/ -->
         <array units="cm-1">0.378
         0.315
         0.178
         </array>
       </property>
       <property dictRef="me:vibFreqs">
        <!-- Taken from http://cccbdb.nist.gov/ -->
```

```
      <array units="cm-1">
        3850.982
        3192.937
        3079.476
        1870.816
        1498.011
        1445.771
        1376.802
        1249.843
        1021.873
        881.846
        595.062
        425.3676
        3153.054
        1500.346
        1083.749
        663.3121
        540.7215
        84.3685
       </array>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
      <scalar>0.943</scalar>
    </property>
    <property dictRef="me:symmetryNumber">
      <scalar>3</scalar>
    </property>
    <property dictRef="me:MW">
      <scalar units="amu">60</scalar>
    </property>
    <property dictRef="me:spinMultiplicity">
      <scalar>1</scalar>
      </property>
    </propertyList>
      <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
 </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="kJ/mol">0.0</scalar>
    </property>
    <property dictRef="me:rotConsts">
      <array units="cm-1">1.44914</array>
    </property>
    <property dictRef="me:symmetryNumber">
      <scalar>2</scalar>
    </property>
    <property dictRef="me:frequenciesScaleFactor">
      <scalar>0.9854</scalar>
    </property>
    <property dictRef="me:vibFreqs">
      <array units="cm-1">1665.4292</array>
    </property>
```

```
        <property dictRef="me:MW">
          <scalar units="amu">32</scalar>
        </property>
        <property dictRef="me:spinMultiplicity">
          <scalar>3</scalar>
        </property>
      </propertyList>
      <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
    </molecule>



    <molecule id="Int1" description="peroxy acetyl O2 adduct">
      <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="O"/>
        <atom id="a7" elementType="O"/>
        <atom id="a8" 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="2"/>
        <bond atomRefs2="a5 a7" order="1"/>
        <bond atomRefs2="a7 a8" order="1"/>
      </bondArray>
      <propertyList>
        <property dictRef="me:ZPE">
          <scalar units="kJ/mol">0.0</scalar>
        </property>
        <property dictRef="me:rotConsts">
          <array units="cm-1">100.1081 100.161 0.3105</array>
        </property>
        <property dictRef="me:symmetryNumber">
          <scalar>1</scalar>
        </property>
        <property dictRef="me:frequenciesScaleFactor">
          <scalar>0.9854</scalar>
        </property>
        <property dictRef="me:vibFreqs">
          <array units="cm-1">138.9727 166.6422 324.9740 506.7799 542.6734
550.0846 733.6783 982.3224 1047.8019 1130.4775 1195.2988 1402.4804 1463.1799
1467.7251 1893.8762 3059.8972 3120.2416 3160.5853</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>
```

```
        <property dictRef="me:deltaEDown">
          <scalar units="cm-1">130.0</scalar>
        </property>
      </propertyList>
      <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
    </molecule>

  </moleculeList>
  <reactionList>
     <reaction id="R1">
      <reactant>
        <molecule ref="acetyl" me:type="modelled"/>
      </reactant>
      <product>
        <molecule ref="CO" me:type="sink"/>
      </product>
      <product>
        <molecule ref="CH3" me:type="sink"/>
      </product>
      <me:transitionState>
        <molecule ref="TSdecomp" me:type="transitionState"/>
      </me:transitionState>

      <me:MCRCMethod>SimpleRRKM</me:MCRCMethod>
    </reaction>
    <reaction id="R2">
<reactant>
<molecule ref="acetyl" me:type="modelled"/>
</reactant>
<reactant>
<molecule ref="O2" me:type="excessReactant"/>
</reactant>
<product>
<molecule ref="Int1" me:type="sink"/>
</product>
<me:MCRCMethod>SimpleBimolecularSink</me:MCRCMethod>
<me:BimolecularLossRateCoefficient>6.2E-11</me:BimolecularLossRateCoefficient>
<me:excessReactantConc>5.8E17</me:excessReactantConc>

</reaction>
  </reactionList>
  <me:conditions>
    <me:bathGas>He</me:bathGas>
    <me:PTs>
      <me:PTpair me:units="Torr" me:P="80" me:T="298." me:precision="qd"/>
      <!--<me:PTpair me:units="Torr" me:P="760" me:T="298." me:precision="qd"/>-->
      <!--<me:PTpair me:units="Torr" me:P="10.06" me:T="298." />
      <me:PTpair me:units="Torr" me:P="15.01" me:T="298." />-->

    </me:PTs>

  </me:conditions>
   <me:InitalPopulation>
   <molecule ref="Acetyl" me:population="1.0"/>
   </me:InitalPopulation>
  <me:modelParameters>
    <!--Specify grain size directly...-->
    <me:grainSize units="cm-1">100</me:grainSize>
    <!--...or by the total number of grains
        <me:numberOfGrains> 50 </me:numberOfGrains>-->
    <!--Specify increased energy range
        <me:maxTemperature>6000</me:maxTemperature>-->
```

```
    <me:energyAboveTheTopHill>210</me:energyAboveTheTopHill>
  </me:modelParameters>
  <me:control>
<me:shortestTimeOfInterest>10e-19</me:shortestTimeOfInterest>

        <me:printSpeciesProfile/>
    <!--<me:testMicroRates />
    <me:testRateConstants />
    <me:printGrainDOS /> -->
    <!--<me:printCellDOS />-->
    <!--<me:printReactionOperatorColumnSums />-->
    <!--<me:printTunnellingCoefficients />-->
        <!--<me:printGrainBoltzmann />
    <me:printGrainkbE />-->

    <me:eigenvalues>6</me:eigenvalues>
  </me:control>
</me:mesmer>
```