Alkyl Chemistry

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Methyl Nitrite and Methyl Nitrate

Methyl Peroxynitrate

PAN and its Homologues
Methyl Nitrite & Methyl Nitrate
Background

Methyl Nitrite (CH$_3$ONO):
- Known as alkyl nitrites (RONO)
- RO + NO + M $\rightarrow$ RONO + M
- Rapid photolysis in the troposphere.

Methyl Nitrate (CH$_3$ONO$_2$):
- Known as alkyl nitrates (RONO$_2$)
- RO + NO$_2$ + M $\rightarrow$ RONO$_2$ + M
- RO$_2$ + NO $\rightarrow$ RO + NO$_2$
- NO$_2$ + hv $\rightarrow$ NO + O
- O + O$_2$ $\rightarrow$ O$_3$
- RO$_2$ + NO $\rightarrow$ RONO$_2$
**Approach**

- *Ab Initio* Calculations using GAUSSIAN 03 software.

- Geometry Optimizations and Frequency Calculations
  
  * Levels of Theory: B3LYP, QCISD, QCISD(T)
  
  * Basis Set: 6-31G(d)
Results: Methyl Nitrite

\[ \text{CH}_3\text{ONO} \ (\text{tc}) \]

\[ \text{CH}_3\text{OHNO} \ (\text{tct}) \]

\[ \text{CH}_3\text{ONOH} \ (\text{tct}) \]
Proton Affinities for the protonated structures of CH$_3$ONO (kcal/mol)

<table>
<thead>
<tr>
<th>Species</th>
<th>B3LYP</th>
<th>QCISD</th>
<th>QCISD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$ONO</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CH$_3$OHNO</td>
<td>190.8</td>
<td>193.1</td>
<td>191.8</td>
</tr>
<tr>
<td>CH$_3$ONOH</td>
<td>175.8</td>
<td>174.3</td>
<td>173.5</td>
</tr>
</tbody>
</table>
Stability of protonated CH$_3$ONO

- CH$_3$ONO (tc)  
  0.0 kcal/mol

- CH$_3$ONOH (tct)  
  173.5 kcal/mol

- CH$_3$OHNO (tct)  
  191.8 kcal/mol
Results: Methyl Peroxynitrite

CH$_3$OONO (tcc)

CH$_3$OHONO (c)  CH$_3$OOHNO (c)  CH$_3$OONOH (t)
Proton Affinities for the protonated structures of CH$_3$OONO (kcal/mol)

<table>
<thead>
<tr>
<th>Species</th>
<th>B3LYP</th>
<th>QCISD</th>
<th>QCISD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OONO</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CH$_3$OHONO</td>
<td>172.2</td>
<td>171.7</td>
<td>172.5</td>
</tr>
<tr>
<td>CH$_3$OOHNO</td>
<td>192.1</td>
<td>195.8</td>
<td>193.1</td>
</tr>
<tr>
<td>CH$_3$OONOH</td>
<td>174.9</td>
<td>171.7</td>
<td>170.9</td>
</tr>
</tbody>
</table>
Stability of protonated CH$_3$OONO

- CH$_3$OONO (tcc): 0.0 kcal/mol
- CH$_3$OONOH (t): 170.9 kcal/mol
- CH$_3$OHONO (C): 172.5 kcal/mol
- CH$_3$OOHNO (c): 193.1 kcal/mol
Conclusions

Our Results:

\[
\text{CH}_3\text{ONO} + \text{H}^+ \rightarrow \text{CH}_3\text{OH} \cdot \text{NO}^+ \quad 191.8 \text{ kcal/mol}
\]

\[
\text{CH}_3\text{OONO} + \text{H}^+ \rightarrow \text{CH}_3\text{OOH} \cdot \text{NO}^+ \quad 193.1 \text{ kcal/mol}
\]

Literature Results:

\[
\text{HONO} + \text{H}^+ \rightarrow \text{H}_2\text{O} \cdot \text{NO}^+ \quad 191.5 \text{ kcal/mol}
\]


\[
\text{CH}_3\text{ONO}_2 + \text{H}^+ \rightarrow \text{CH}_3\text{OH} \cdot \text{NO}_2^+ \quad 176.9 \text{ kcal/mol}
\]

Methyl Peroxynitrate
Alkyl Peroxynitrates are formed from the reaction of RO₂ with NO₂:

\[
\text{RO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{ROONO}_2 + \text{M}
\]

They can go on to form alkyl nitrates (RONO₂) and alkyl nitrites (RONO).

Methyl Peroxynitrate (CH₃OONO₂) plays a role in the NOₓ budget and in urban smog formation.
Approach

- *Ab Initio* Calculations using GAUSSIAN 03 software.

- Geometry optimizations and Frequency Calculations
  
  * Levels of Theory: B3LYP, QCISD, QCISD(T)
  
  * Basis Set: 6-31G(d), 6-311++G(2d,2p),
    6-311++G(2df,2p), 6-311++G(3df,3pd)

- Composite Methods: G2(MP2), CBS-Q, CBS-APNO
Results: Methyl Peroxynitrate

\[
\begin{align*}
\text{CH}_3\text{OONO}_2 & \\
\text{CH}_3\text{OHONO}_2 & \\
\text{CH}_3\text{OONOO}_2 & \\
\text{CH}_3\text{OOHNO}_2 & \\
\text{CH}_3\text{OONO}_2\text{H} & 
\end{align*}
\]
### Proton Affinities for the protonated structures of CH$_3$OONO$_2$ (kcal/mol)

<table>
<thead>
<tr>
<th>Species</th>
<th>B3LYP</th>
<th>QCISD</th>
<th>QCISD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OONO$_2$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CH$_3$OHONO$_2$</td>
<td>163.7</td>
<td>160.9</td>
<td>162.9</td>
</tr>
<tr>
<td>CH$_3$OOHNO$_2$</td>
<td>173.7</td>
<td>173.5</td>
<td>174.0</td>
</tr>
<tr>
<td>CH$_3$OONO$_2$H</td>
<td>163.9</td>
<td>163.7</td>
<td>162.2</td>
</tr>
</tbody>
</table>
Proton Affinities for the protonated structure of CH₃OONO₂ (kcal/mol)

<table>
<thead>
<tr>
<th>QCISD(T)</th>
<th>CH₃OONO₂</th>
<th>CH₃OONHO₂</th>
<th>CH₃OHONO₂</th>
<th>CH₃OONO₂H</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31G(d)</td>
<td>0.0</td>
<td>174.0</td>
<td>162.9</td>
<td>162.2</td>
</tr>
<tr>
<td>6-311++G (2d,2p)</td>
<td>0.0</td>
<td>178.8</td>
<td>165.0</td>
<td>164.8</td>
</tr>
<tr>
<td>6-311++G (2df,2p)</td>
<td>0.0</td>
<td>177.9</td>
<td>163.9</td>
<td>164.3</td>
</tr>
<tr>
<td>6-311++G (3df,3pd)</td>
<td>0.0</td>
<td>178.8</td>
<td>164.6</td>
<td>165.0</td>
</tr>
</tbody>
</table>
Proton Affinities for the lowest energy structure of $\text{CH}_3\text{OOONO}_2$ (kcal/mol)

<table>
<thead>
<tr>
<th>Composite Methods</th>
<th>$\text{CH}_3\text{OOHNO}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G2(MP2)</td>
<td>177.2</td>
</tr>
<tr>
<td>CBS-Q</td>
<td>175.6</td>
</tr>
<tr>
<td>CBS-APNO</td>
<td>176.8</td>
</tr>
</tbody>
</table>
Stability of protonated \( \text{CH}_3\text{OONO}_2 \)

- \( \text{CH}_3\text{OONO}_2 \): 0.0 kcal/mol
- \( \text{CH}_3\text{OHONO}_2 \): 164.6 kcal/mol
- \( \text{CH}_3\text{OONO}_2\text{H} \): 165.0 kcal/mol
- \( \text{CH}_3\text{OOHNO}_2 \): 178.8 kcal/mol
Comparison of Proton Affinities for the XOONO₂ species

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis Set</th>
<th>CH₃OONO₂ (kcal/mol)</th>
<th>HOONO₂³ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QCISD(T)</td>
<td>6-31G(d)</td>
<td>174.0</td>
<td>170.0</td>
</tr>
<tr>
<td></td>
<td>6-311++G(2d,2p)</td>
<td>178.8</td>
<td>175.4</td>
</tr>
<tr>
<td></td>
<td>6-311++G(2df,2pd)</td>
<td>177.9</td>
<td>174.2</td>
</tr>
<tr>
<td></td>
<td>6-311++G(3df,3pd)</td>
<td>178.8</td>
<td>175.1</td>
</tr>
</tbody>
</table>

# Comparison of Proton Affinities

<table>
<thead>
<tr>
<th>Species</th>
<th>PA (kcal/mol)</th>
<th>Species</th>
<th>PA (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃ONO</td>
<td>191.8</td>
<td>HONOₐ</td>
<td>191.5</td>
</tr>
<tr>
<td>CH₃OONO</td>
<td>193.1</td>
<td>HOONOₖ</td>
<td>182.1</td>
</tr>
<tr>
<td>CH₃ONO₂</td>
<td>176.9 ± 5</td>
<td>HONO₂ₖ</td>
<td>182.5</td>
</tr>
<tr>
<td>CH₃OONO₂</td>
<td>178.8</td>
<td>HOONO₂ₖ</td>
<td>175.1</td>
</tr>
</tbody>
</table>

Conclusions

- We find a general trend for the proton affinities of the XONO$_2$ and XOONO$_2$ species.

- We find a methyl effect for these species as well.
PAN and its Homologues
Background

- Peroxyacetyl Nitrate or PAN (CH$_3$C=OO$_2$NO$_2$) is the most abundant and simplest member of the peroxyacyl nitrates.

- PAN is produced from the photochemical reactions of hydrocarbons and nitrogen oxides in the atmosphere:

$$\text{CH}_3\text{CO}_3 + \text{NO}_2 + \text{M} \leftrightarrow \text{CH}_3\text{CO}_3\text{NO}_2 + \text{M}$$
Background

- GC-ECD, luminol chemiluminescence detector and FTIR are among some of the ways in which PAN has been measured.

- PANs that have been observed are typically at concentrations much less than PAN and include: PPN, MPAN, APAN, and PFN.

  - PPN: \( \text{CH}_3\text{CH}_2\text{C} = \text{OO}_2\text{NO}_2 \)
  - MPAN: \( \text{CH}_2 = \text{C(CH}_3\text{)}\text{C} = \text{OO}_2\text{NO}_2 \)
  - APAN: \( \text{CH}_2 = \text{C(H)}\text{C} = \text{OO}_2\text{NO}_2 \)
  - PFN: \( \text{HC} = \text{OO}_2\text{NO}_2 \)
Approach

- *Ab Initio* Calculations using GAUSSIAN 03 software.

- Geometry Optimizations and Frequency Calculations
  
  * Composite Methods: G2(MP2) & CBS-Q

  * Basis Set: 6-311+G(3df,2p)
Results

Unprotonated Structure

Protonated Structures

Structure 1

Structure 2
Results

Unprotonated Structure

Protonated Structures

Structure 1

Structure 2

APAN

MPAN
Proton Affinities of PAN, PPN, MPAN, APAN, PFN & their protonated structures (kcal/mol)

<table>
<thead>
<tr>
<th>Species</th>
<th>G2(MP2)</th>
<th>CBS-Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Structure 1</td>
<td>180.1</td>
<td>179.4</td>
</tr>
<tr>
<td>Structure 2</td>
<td><strong>185.4</strong></td>
<td><strong>184.9</strong></td>
</tr>
<tr>
<td>PPN</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Structure 1</td>
<td>181.7</td>
<td>182.1</td>
</tr>
<tr>
<td>Structure 2</td>
<td><strong>185.8</strong></td>
<td><strong>186.2</strong></td>
</tr>
<tr>
<td>MPAN</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Structure 1</td>
<td>185.2</td>
<td>185.4</td>
</tr>
<tr>
<td>Structure 2</td>
<td><strong>186.2</strong></td>
<td><strong>186.1</strong></td>
</tr>
<tr>
<td>APAN</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Structure 1</td>
<td>183.4</td>
<td>183.2</td>
</tr>
<tr>
<td>Structure 2</td>
<td><strong>185.9</strong></td>
<td><strong>185.4</strong></td>
</tr>
<tr>
<td>PFN</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Structure 1</td>
<td>170.9</td>
<td>170.3</td>
</tr>
<tr>
<td>Structure 2</td>
<td><strong>182.6</strong></td>
<td><strong>181.9</strong></td>
</tr>
</tbody>
</table>

Structure 1: Structure protonated on the oxygen of the carbonyl group

Structure 2: Structure protonated on the tertiary oxygen
Conclusions

- We find the lowest energy structure throughout the PANs to be protonated at the tertiary oxygen, which results in a complex between RC=OOOOH and NO$_2^+$.

- We find a trend in the proton affinities with respect to the R- group.
Acknowledgements

- Dr. Joseph S. Francisco
- Dr. Jeff Gaffney
- Dr. Nancy Marley
- Milt Constantin & Alicia Wells
- GCEP/GREF