Failures and Limitations of Quantum Chemistry for Two Key Problems in the Atmospheric Chemistry of Peroxy Radicals

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From Quantum Chemistry to Kinetics

Calculate Coulombic energy of a molecular structure
Optimize structure to energy minimum (Reactant/Product)
Optimize structure to Transition State (TS)

\[ E_a \text{ from } E_{TS} - E_{Reac} \quad \Delta E_r \text{ from } E_{Prod} - E_{Reac} \]

1.4 kcal/mole error in \( E_a \) is a factor of 10 in \( k \) at 298 K

Quantum chemistry: \( k \) and branching ratios can’t compete with experiment.
Mechanism #1  RONO$_2$ Formation

ROO$\cdot$ + NO  $\rightarrow$  RONO$_2$  (up to 30%)

Proposed Mechanism:  *(Atkinson, Carter, & Winer, 1983)*

ROO$\cdot$ + NO  $\rightarrow$  ROON=O$^\ast$  (1)

(2a)  

(2b)  

Transition State
What is the Energy of the TS?

- Calculated TS above ROO + NO by 2-30 kcal/mole
Electronic Structure of TS

\[ \text{ROON}=\text{O} \rightarrow \text{RONO}_2 \]
All electrons paired (\(\downarrow\uparrow\))

All published TS’s assume all electrons paired (\(\downarrow\uparrow\))

We asked:
Is it the lowest energy state?
\textbf{No!} \uparrow\uparrow

? unphysical constraint \(\Rightarrow\) meaningless results
Conclusions: RONO₂ Formation

TS structure: multiconfigurational treatment
   [Sumathi and Peyerimhoff, 2003] might work, needs testing to verify correct TS

Energy of TS (Eₐ): needs dynamic electron correlation

Variational RRKM for “loose” TS?
Mechanism #2 \( \text{ROO} \cdot + \text{ROO} \cdot \)

\[
\text{CH}_3\text{OO} \cdot + \text{CH}_3\text{OO} \cdot \rightarrow \text{CH}_3\text{O} \cdot + \text{O}_2 + \text{CH}_3\text{O} \cdot \quad (a)
\]

\[
\rightarrow \text{CH}_3\text{OH} + \text{O}_2 + \text{CH}_2=\text{O} \quad (b)
\]

Proposed Mechanism [Russell, 1957]
Reactions of ROOOOR
(Ghigo, Maranzana, and Tonachini*, 2003)

\[ \text{CH}_3\text{OOOOCCH}_3 \rightarrow \text{Products} \]

2 \text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{=O}
Model of Branching Ratio
(Ghigo, Maranzana, and Tonachini*, 2003)

Tyndall, et al, 2001
The Utility of Quantum Chemistry

- pruning branches
- testing new branches
- substituent effects/SARs (semi-quantitatively)
Conclusions: ROO• + ROO•

System of 4 unpaired electrons!
• needs Tonachini’s approach (special expertise)
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Multiconfigurational Treatment of Structure

*Sumathi and Peyerimhoff, 2003:* Is it the right structure?

Energy from high level theory using structure from low CAS-PT2//CASSCF
Pushing Electrons $\Rightarrow$ “Tight” TS
Reactions of ROOOR
(Ghigo, Maranzana, and Tonachini*, 2003)
(Above authors with CAS-PT2, my group with DFT)

\[ \text{CH}_3\text{OOOOCCH}_3 \rightarrow \text{Products} \]

Loosely-bound complex \( \rightarrow 2 \text{CH}_3\text{O} \cdot + \text{O}_2 \)
Conservation of Electron Spin

\[
\begin{align*}
\ce{H & H} & \ce{O} & \ce{H & H} \\
\uparrow & & \uparrow & \downarrow O=O \\
\ce{H} & \ce{O} & \ce{H} & \ce{H} & \ce{H} \\
\end{align*}
\]

4 unpaired electrons
net spin = 0

\[
\ce{CH_3OH + O_2 + CH_2=O}
\]

Electron Spin of Products

O₂ in excited (↓ ↑) state ??
If O₂ in ground (↓ ↓) state, then
CH₂=O in excited (↑ ↑) state

Either product set \textit{kinetically unfavorable}
Spin Flip Needed

Net Spin = 0

Net Spin 1

2 CH₃O• → CH₃OH + CH₂=O