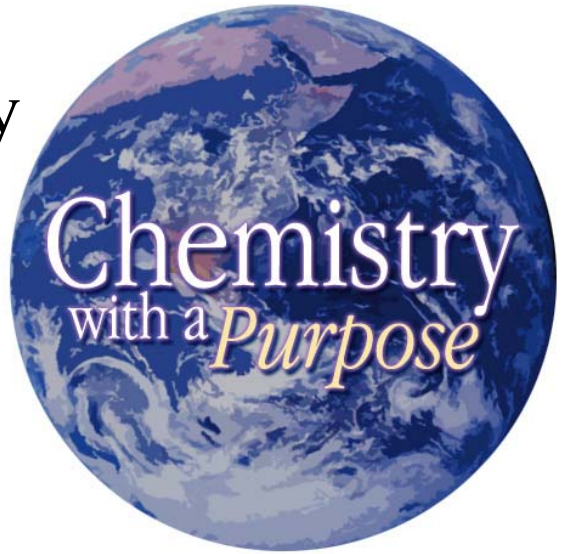
Failures and Limitations of Quantum Chemistry for Two Key Problems in the Atmospheric Chemistry of Peroxy Radicals

Theodore S. Dibble

Chemistry Department,
SUNY-Environmental Science and Forestry
Syracuse, NY



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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 from $E_{TS} - E_{Reac}$ ΔE_r from $E_{Prod} - E_{Reac}$

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

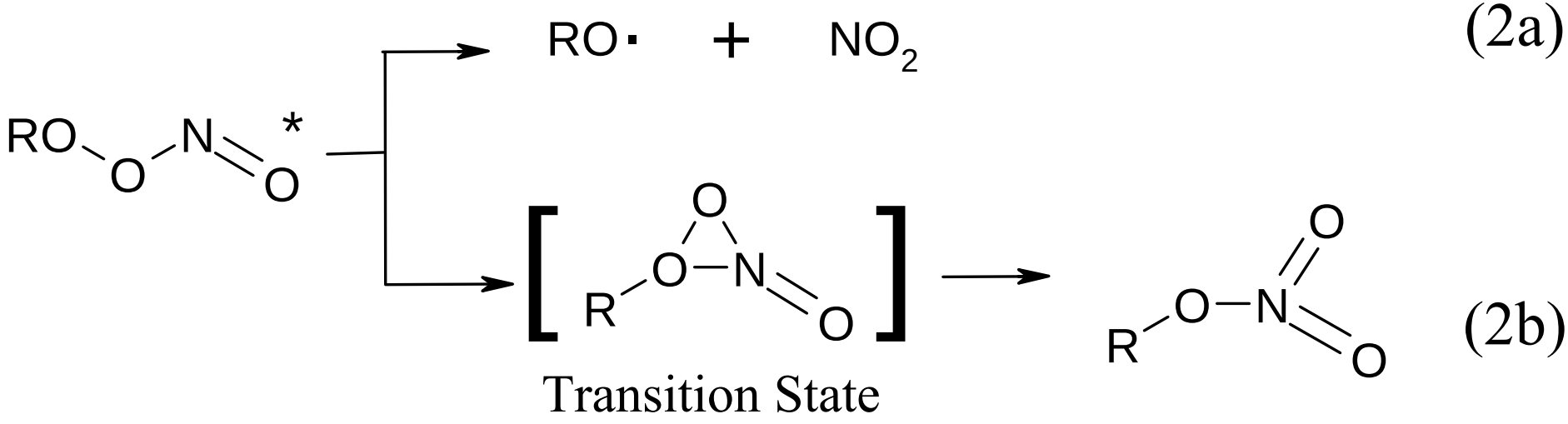
Quantum chemistry: k and branching ratios
can't compete with experiment.

Mechanism #1 $RONO_2$ Formation

$$ROO\bullet + NO \rightarrow RONO_2 \quad \text{(up to 30\%)}$$

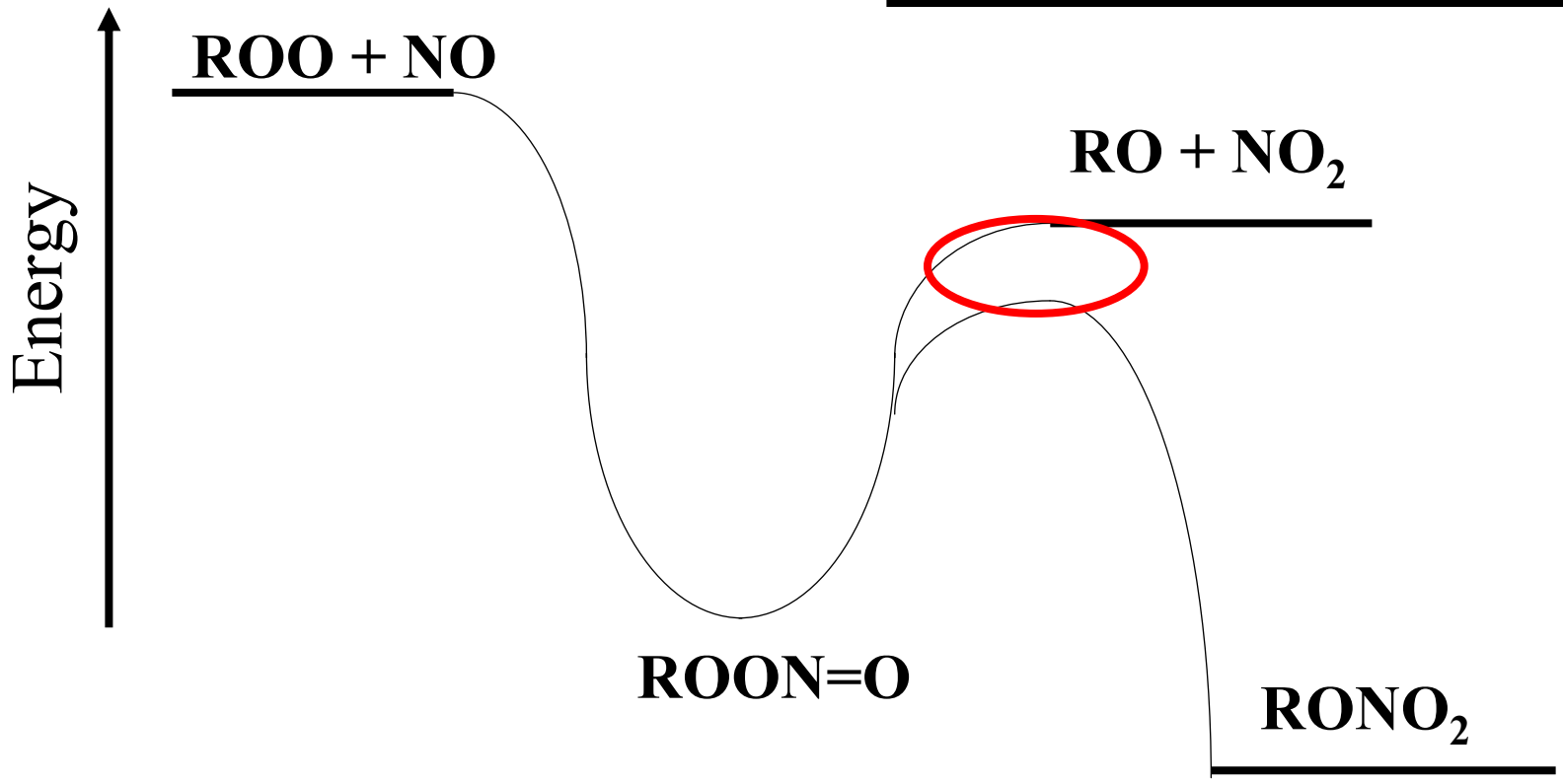
Proposed Mechanism: *(Atkinson, Carter, & Winer, 1983)*

$$ROO\bullet + NO \rightarrow ROON{=}O^* \quad (1)$$



What is the Energy of the TS?

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



Electronic Structure of TS

$$ROON{=}O \rightarrow RONO_2$$

All electrons paired (↓↑)

<u>All published TS's assume all electrons paired (↓↑)</u>

We asked:

Is it the lowest energy state?

No! ↑↑

? unphysical constraint ⇒ meaningless results

Conclusions: $RONO_2$ Formation

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

Energy of TS (E_a): needs dynamic electron correlation

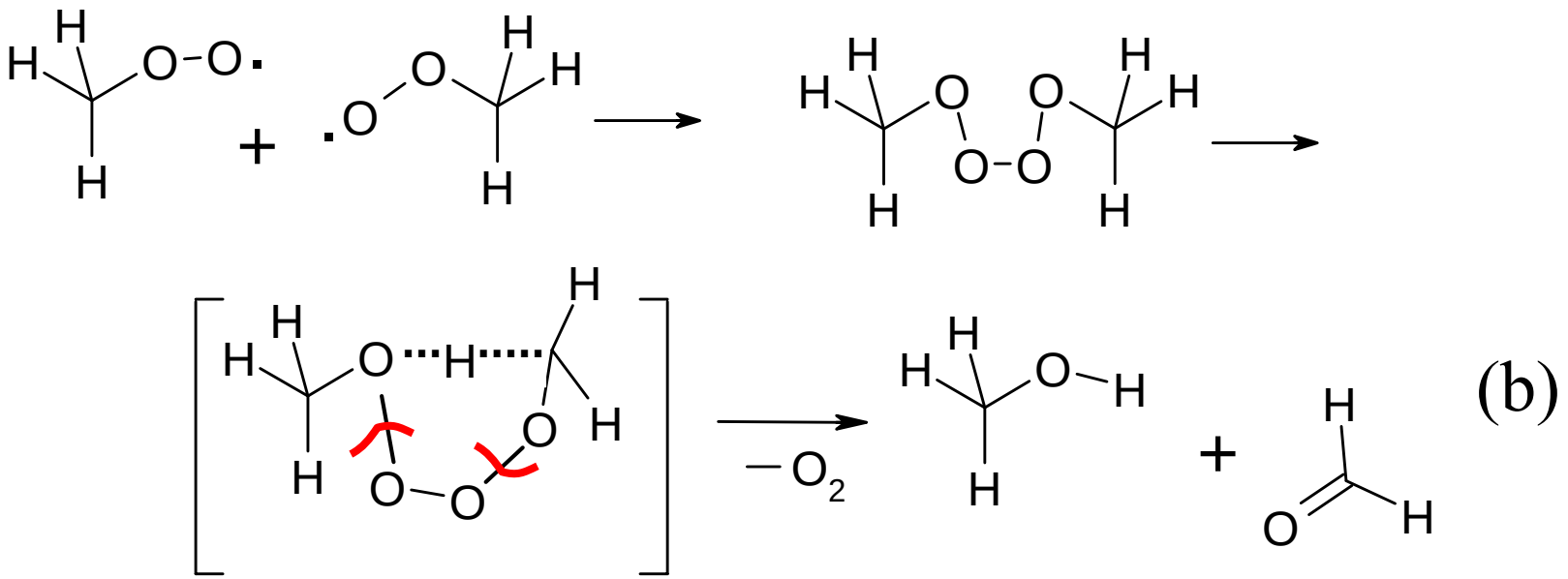
Variational RRKM for "loose" TS ?

Mechanism #2 ROO• + ROO•

$CH_3OO\bullet + CH_3OO\bullet \rightarrow CH_3O\bullet + O_2 + CH_3O\bullet$ (a)

$\rightarrow CH_3OH + O_2 + CH_2{=}O$ (b)

Proposed Mechanism [*Russell*, 1957]



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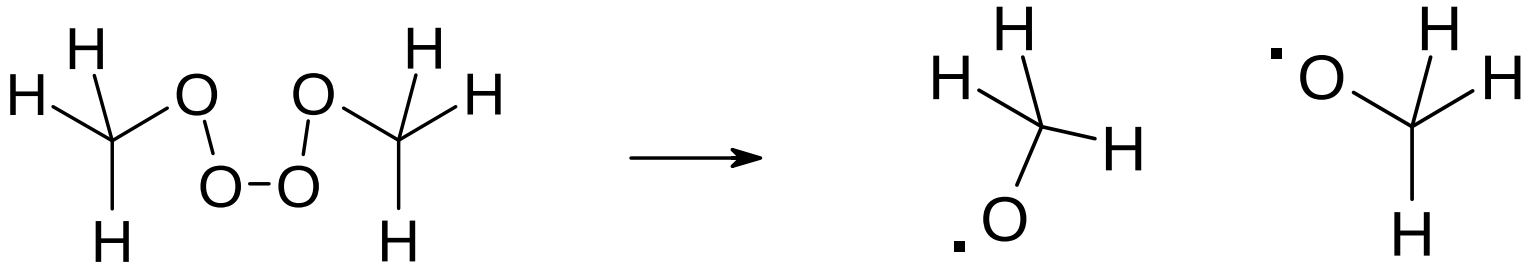
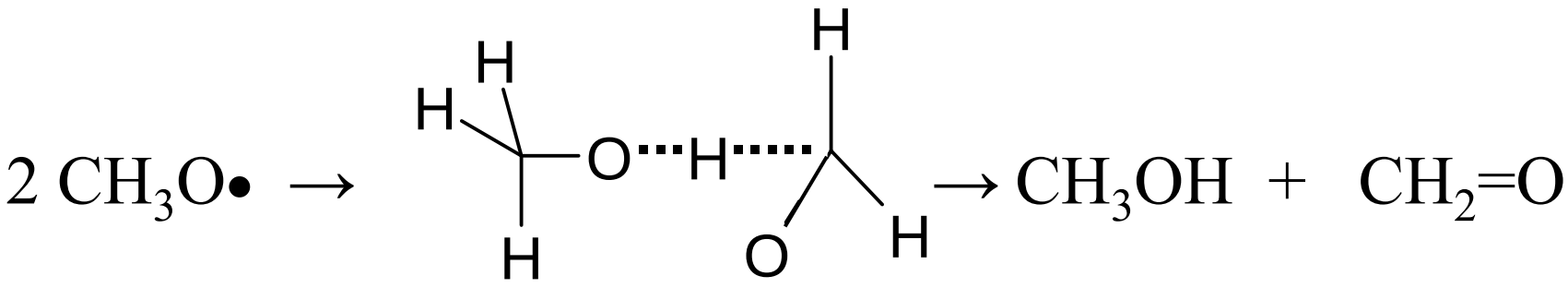
Reactions of ROOOOR

(Ghigo, Maranzana, and Tonachini*, 2003)

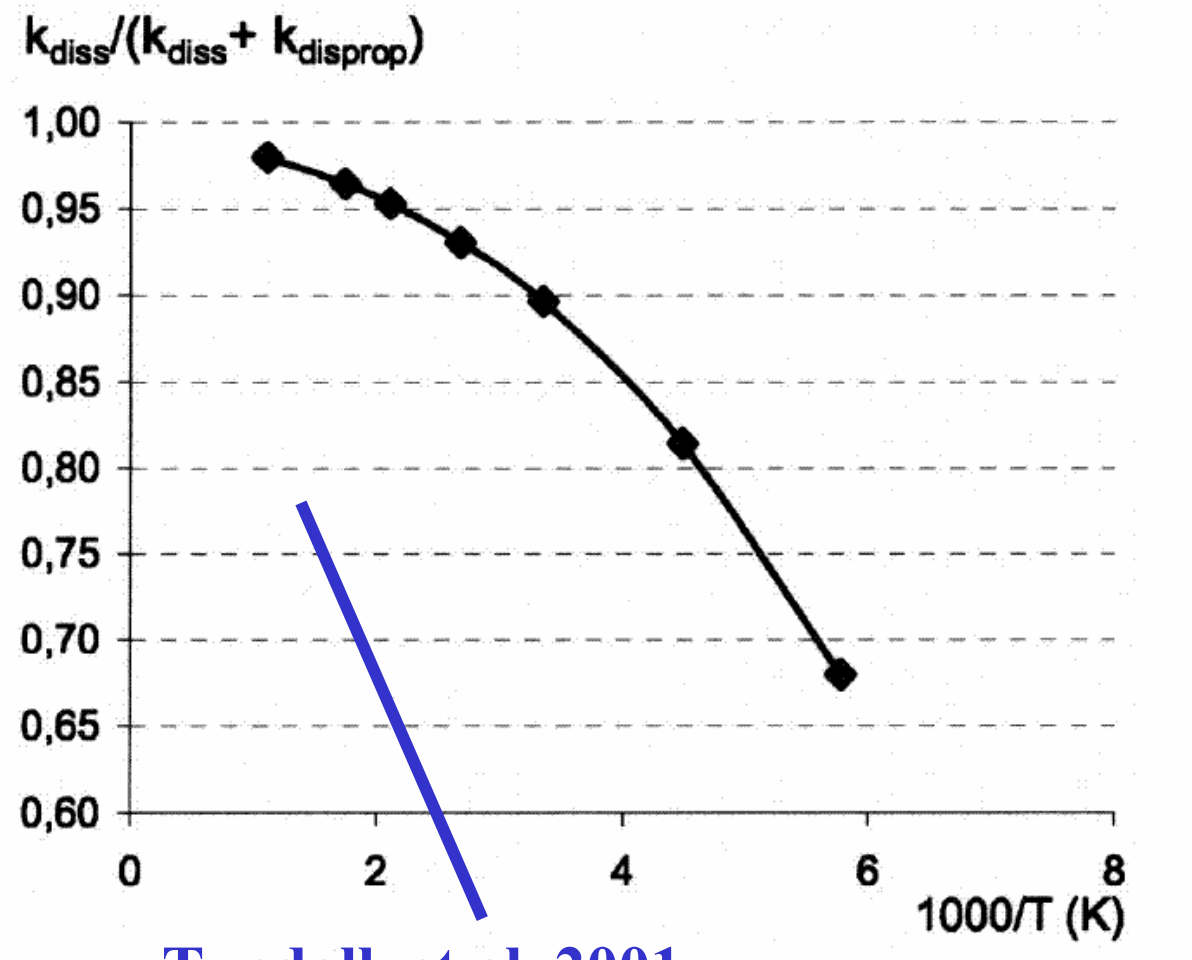
$CH_3OOOOCH_3 \not\rightarrow$ Products





Model of Branching Ratio

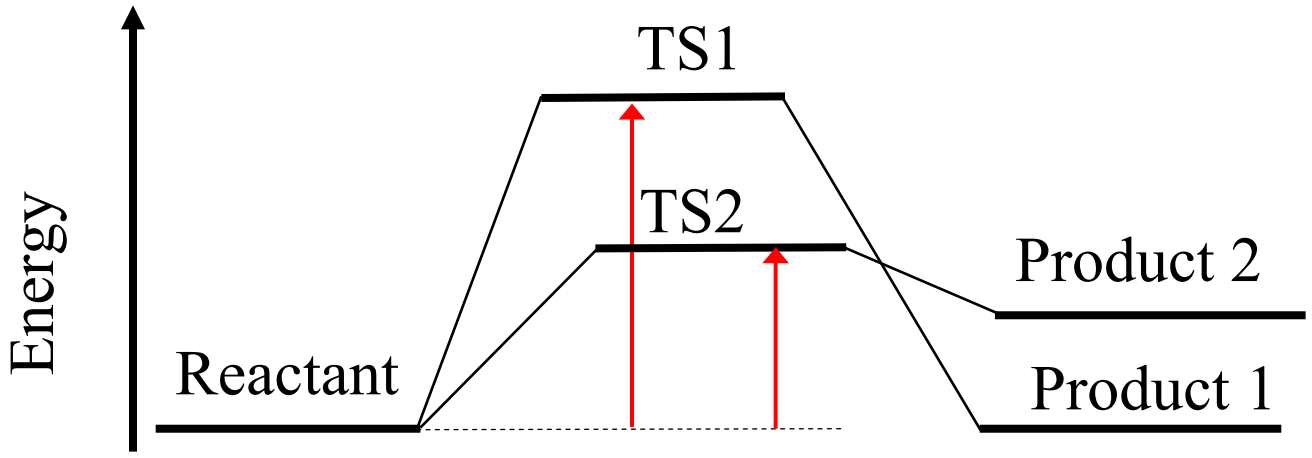
(Ghigo, Maranzana, and Tonachini*, 2003)



Tyndall, et al, 2001

The Utility of Quantum Chemisty

- pruning branches
- testing new branches
- substituent effects/SARs (semi-quantitatively)



Conclusions: ROO• + ROO•

System of 4 unpaired electrons!

- needs Tonachini's approach (special expertise)

Acknowledgements

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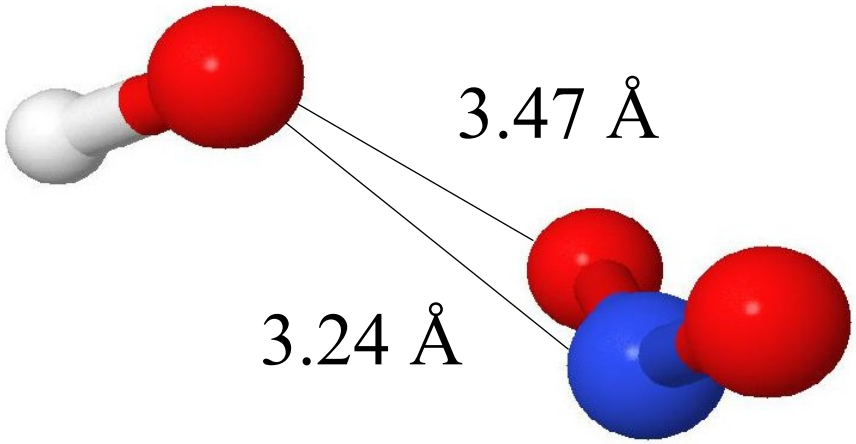
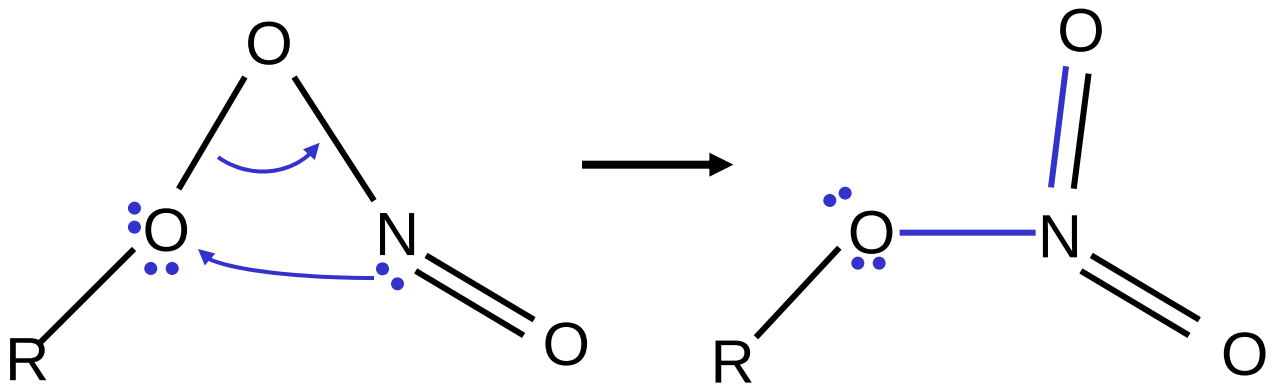
Multiconfigurational Treatment of Structure

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



Energy from high level theory using structure from low CAS-PT2//CASSCF

Pushing Electrons ⇒ “Tight” TS



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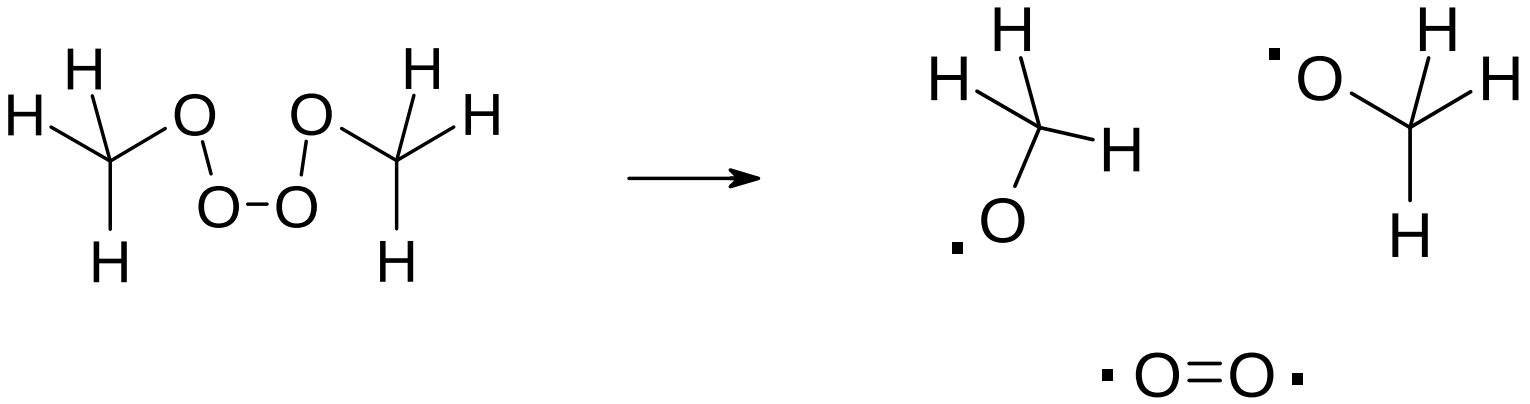
Reactions of ROOOOR

(Ghigo, Maranzana, and Tonachini*, 2003)

(Above authors with CAS-PT2, my group with DFT)

$CH_3OOOOCH_3 \not\rightarrow$ Products



Loosely-bound complex $\rightarrow$ 2 $CH_3O\bullet$ + O_2

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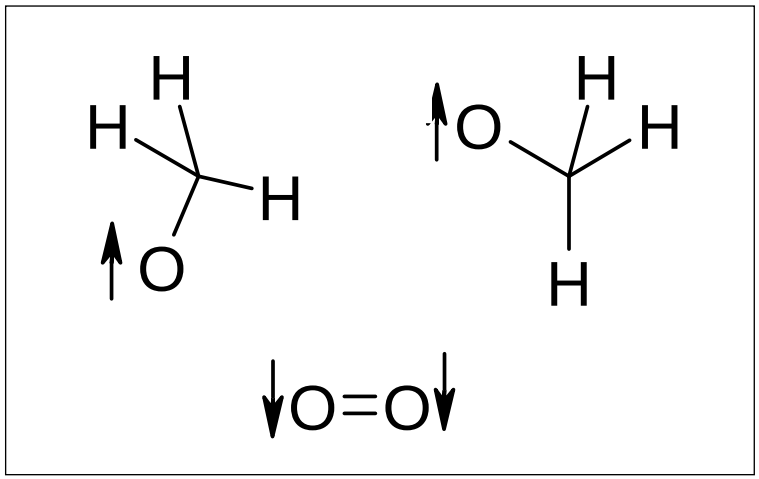
Conservation of Electron Spin



$\longrightarrow$ $CH_3OH + O_2 + CH_2{=}O$

4 unpaired electrons

net spin = 0

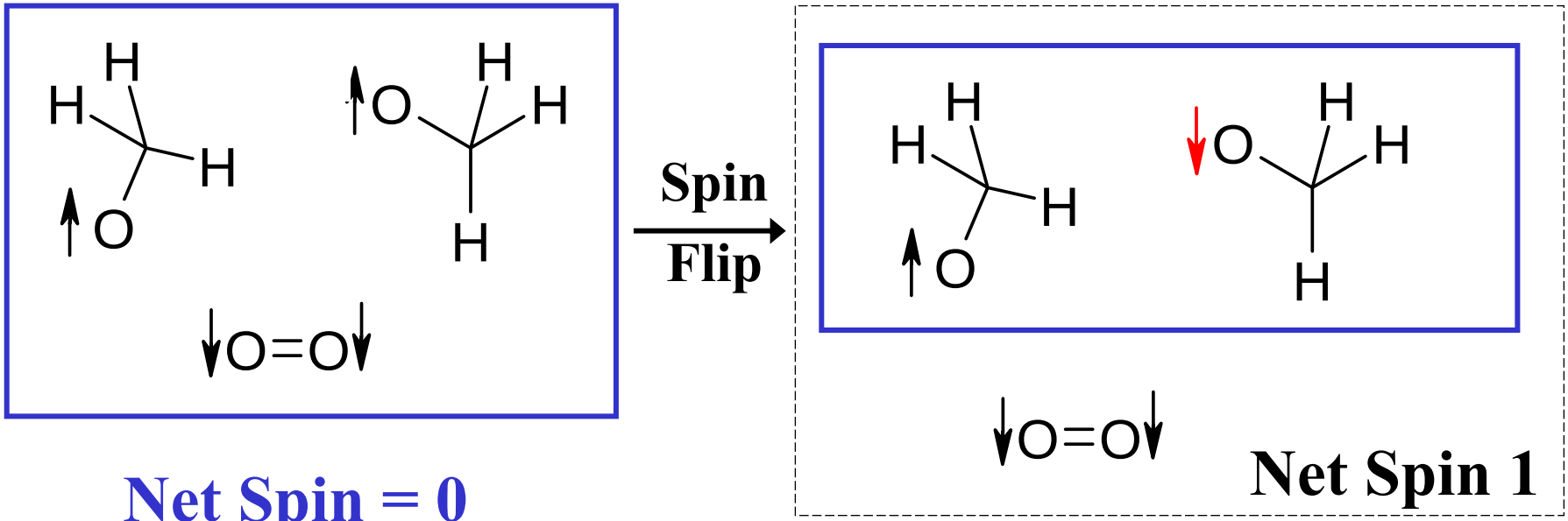
Electron Spin of Products

O_2 in excited ($\downarrow\uparrow$) state ??

If O_2 in ground ($\downarrow\downarrow$) state, then $CH_2{=}O$ in excited ($\uparrow\uparrow$) state

Either product set kinetically unfavorable

Spin Flip Needed



Net Spin = 0