Evaluating mechanisms for dimer formation from $\text{RO}_2 + \text{RO}_2$ reactions

7th December 2018

Theo Kurtén

Department of Chemistry
University of Helsinki, Finland
Co-workers and organizations

- **University of Helsinki, chemistry**: Noora Hyttinen, Siddharth Iyer, Vili Salo, Galib Hasan, Rashid Valiev
- **University of Helsinki, physics**: Matti Rissanen, Mikael Ehn & group
- **University of Copenhagen**: Henrik Kjaergaard, Kristian Holten Møller, Rasmus Otkjaer, Helene Jakobsen
- **CalTech**: Paul Wennberg & group
- **UC Irvine**: Danielle Draper, Jim Smith & group
- **Reed College, Portland**: Juliane Fry & group
- **University of Washington, Seattle**: Emma D’Ambro, Joel Thornton & group
- Also thanks to **Michelle Coote** for helpful discussions, and to **NSF** and **UCI** for funding my trip!
Two well-known channels for gas-phase $\text{RO}_2 + \text{RO}_2$:

1) $\text{RO} + \text{RO} + \text{O}_2$
2) $\text{R}=\text{O} + \text{ROH} + \text{O}_2$

Also 3) $\text{ROOR} + \text{O}_2$, but little evidence in gas phase for small $\text{R}$.

For larger $\text{R} \geq 3 \text{ C}$, ROOR formation recently unambiguously demonstrated (e.g. Berndt et al., Angew. Chem., 57, 3820, 2018).

ROOR dimers likely key in aerosol formation from e.g. monoterpenes autoxidation, as they are the genuine “ELVOC”.

Molecular-level $\text{RO}_2 + \text{RO}_2$ mechanism remains a mystery, and a “challenge for computational methods” (Dibble 2008).

$\text{RO}_2 + \text{RO}_2$ generally believed (since 1957) to proceed via a $\text{RO}_4\text{R}$ tetroxide intermediate, but what then?
• Russell (1957): different RO$_2$ + RO$_2$ channels correspond to different geometries and/or decomposition pathways of RO$_4$R.

• Computational studies using DFT geometries do find multiple RO$_4$R decomposition pathways, but typically with very high barriers (especially for ROOR), and overall rates and/or product yields quite different from experiments.

• Ghigo et al (JCP 2003) and Lee et al (PCCP 2016) propose a different mechanism where the branching comes after RO$_4$R decomposition.
Lee et al (PCCP 2016) proposed mechanism

\((DFT + CCSD(T) + tricks)\)

RO₄R forms on a singlet surface (all electrons paired).

This TS not found in other/earlier studies.
Lee *et al* (PCCP 2016) proposed mechanism *(DFT + CCSD(T) + tricks)*

- **RO**$_4$R forms on a **singlet** surface (all electrons paired).
- O-O bonds split to form O$_2$, and two RO, bound in a “**cage**”. All reaction channels go through this cage.
Lee et al (PCCP 2016) proposed mechanism (\textit{DFT + CCSD(T) + tricks})

- RO\textsubscript{4}R forms on a \textbf{singlet} surface (all electrons paired).
- O-O bonds split to form O\textsubscript{2}, and two RO, bound in a "\textbf{cage}". All reaction channels go through this cage. \textbf{O\textsubscript{2} has a triplet} ground state (2 unpaired electrons), thus the two RO need to be coupled as a \textbf{triplet} (to keep whole system a singlet).
Lee et al (PCCP 2016) proposed mechanism

\((DFT + CCSD(T) + \text{tricks})\)

- \(\text{RO}_4\text{R}\) forms on a \textbf{singlet} surface (all electrons paired).
- O-O bonds split to form \(\text{O}_2\), and two \(\text{RO}\), bound in a "\textbf{cage}". All reaction channels go through this cage.
- \(\text{O}_2\) has a \textbf{triplet} ground state (2 unpaired electrons), thus the two \(\text{RO}\) need to be coupled as a \textbf{triplet} (to keep whole system a singlet).
- Recombination to \(\text{ROOR}\) (singlet) thus \textbf{spin-forbidden}, and needs an \textbf{intersystem crossing} (relativistic effect). ISC rate determines the dimer yield.
Lee et al (PCCP 2016) proposed mechanism

(\textit{DFT + CCSD(T) + tricks})

- \(\text{RO}_4\text{R}\) forms on a \textbf{singlet} surface (all electrons paired).
- O-O bonds split to form \(\text{O}_2\), and two \(\text{RO}\), bound in a “\textbf{cage}”. All reaction channels go through this cage.
- \(\text{O}_2\) has a triplet ground state (2 unpaired electrons), thus the two \(\text{RO}\) need to be coupled as a \textbf{triplet} (to keep whole system a singlet).
- Recombination to \(\text{ROOR}\) (singlet) thus \textbf{spin-forbidden}, and needs an intersystem crossing (relativistic effect). \textbf{ISC rate determines the dimer yield}.
- \(\text{RO} + \text{RO}\) yield determined by \(\text{RO}...\text{RO binding, carbonyl} + \text{ROH}\) yield controlled by the bimolecular H-abstraction rate.
Our analysis of the mechanism part 1: RO₄R barriers

- Overall **barrier** in Lee *et al.* too high compared to expt. rates.
- ΔE for RO₂ + RO₂ → RO₄R reaction ≈ -15 kcal/mol
  - CCSD(T)-F12/VDZ-F12 for R = CH₃, CH₃CH₂, (CH₃)₂CH, DFT on larger
- Multireference calculations find transition states for both RO₄R formation and decomposition (like Lee), **but** (unlike Lee) both are within a few kcal/mol of the RO₄R.
  - XMC-QDPT2(10,8) energies on CASSCF(10,8) geometries with a 6-311++G** basis set, on the overall singlet PES.
- TSs thus likely “**submerged barriers**” w.r.t. reactants.
  - R = CH₃, CH₃CH₂, (CH₃)₂CH, (CH₃)₃C, BuOH, CH₃C(O)CH₂, BuONO₂
  - Ordering qualitatively agrees with expts, e.g. higher barrier for t-but RO₂
  - Agrees with Ghigo (2003) on CH₃O₄CH₃ decomposition.
- Rate-limiting step may be RO₄R **formation** not decomposition
Energies (kcal/mol) relative to RO$_4$R

(XMC-QDPT2 at CASSCF(10,8) geometry)
Our analysis of the mechanism part 2: $^3$(RO…RO) fate

- $O_2$ in RO…O$_2$…RO very weakly bound: we model subsequent reactions with RO…RO.
- $^3$(CH$_3$O…CH$_3$O) weakly bound with respect to CH$_3$O + CH$_3$O; ∼5 kcal/mol according to both CCSD(T)//DFT and XMC-QDPT2.
- $^3$(RO…RO) binding increases with complexity of R, but surprisingly slowly (intra)molecular H-bonding in RO.
- H-shift barrier also low; 6…9 kcal/mol for $^3$(CH$_3$O…CH$_3$O).
- Both RO + RO and R=O + ROH formation is thus likely to be very fast – can ISC really compete?
ISC rate for $^3$(CH$_3$O…CH$_3$O)

- ISC rate depends on spin-orbit coupling (SOC) and energy gap between S and T states (also Huang-Rhys or Franck-Condon factors for the vibrational part; these are less important in this case).
- We have used XMC-QDPT2 excitation energies (4 singlet & 4 triplet states) and spin-orbit couplings at the MCSCF level using the one-electron Breit-Pauli operator, with a 10,8 active space & the 6-311++G** basis.
- For $^3$(CH$_3$O…CH$_3$O), both the SOC and the energy gap between $T_1$ and $S_1$ are small; 0.3 and 25 cm$^{-1}$, respectively. This gives an ISC rate of about $10^8$ s$^{-1}$.
- SOC (and ISC) much larger between $T_1$ and $S_2$ or $S_3$: up to $10^{12}$ s$^{-1}$.
- Probably related to El Sayed’s rule: $T_1$ and $S_1$ electron configurations are too similar (giving low SOC).
$^3(\text{CH}_3\text{O}...\text{CH}_3\text{O})$ electronic states

Energy, cm$^{-1}$

$K_{ISC} = 4 \times 10^5$ s$^{-1}$
$K_{ISC} = 4 \times 10^{11}$ s$^{-1}$
$K_{ISC} = 4 \times 10^{12}$ s$^{-1}$

$k_{IC} = 10^{12}$ to $10^{14}$ s$^{-1}$
$k_{ISC} = 3 \times 10^8$ s$^{-1}$
ISC rate for larger $^3(\text{RO} \ldots \text{RO})$

- Larger $^3(\text{CH}_3\text{O} \ldots \text{CH}_3\text{O})$ have multiple conformers. Our main test system: $^3(\text{CH}_3\text{C(O)}\text{CH}_2\text{O} \ldots \text{CH}_3\text{C(O)}\text{CH}_2\text{O})$.
- Smallest system for which ROOR formation unambiguously observed (Berndt et al., 2018)

- ISC between $T_1$ and $S_1$ varies enormously between conformers: from 1 to $10^9$ s$^{-1}$ (depending on distance between radical centers)
- ISC between $T_1$ and $S_2/S_3$ varies less, always around $10^8$ s$^{-1}$.  

ISC rates roughly around $10^8$ s$^{-1}$ found also for large $^3$(RO…RO) from e.g. alpha-pinene + O$_3$ and trimethylbenzene + OH (also 1-butene + OH)

Note: arbitrary conformers, no sampling (yet)
Conclusion: ROOR probably forms by intersystem crossing

- Ghigo/Lee mechanism for ROOR formation from RO₂ + RO₂ seems promising, with a few modifications:
  - Entrance-channel barrier exists, and might be rate-limiting
  - Barriers for RO₄R formation and decomposition are probably all well below RO₂ + RO₂ in E_{elec}.
- ISC rates for \(3(\text{RO}...\text{RO})\) likely to be at least \(10^8\) s\(^{-1}\), and involve not only T\(_1\) and S\(_1\) but also S\(_2\), S\(_3\) states.
- Fragmentation and H-shift channels of \(3(\text{RO}...\text{RO})\) will also be very fast (barriers < 10 kcal/mol & excess energy from RO₂ + RO₂, however part of excess likely removed by O₂ loss).
- Statistical theories (based on TST) may not work very well here: a challenge but also an opportunity for dynamic simulations?
Thank you for your attention!
Extra slide 1: CASSCF(10,8) orbitals for MeO$_4$Me
(similar orbitals picked for all other RO$_4$R)
Extra slide 2: CASSCF(10,8) orbitals for $^3$(CH$_3$O…CH$_3$O)

Note: the fact that a 10-electron, 8-orbital active space is appropriate for describing both the formation/decomposition of RO$_4$R and the intersystem crossings in $^3$(RO…RO) is coincidental. The two 10,8 spaces are not ”related”, except that both of course involve some of the same orbitals of the O atoms.
Extra slide 3: CASSCF(10,8) orbitals for one conformer of
$^3(\text{CH}_3\text{C(O)}\text{CH}_2\text{O}\ldots\text{CH}_3\text{C(O)}\text{CH}_2\text{O})$

*similar orbitals picked for all other $^3(\text{RO}\ldots\text{OR})$*
Extra slide 4: Energy levels and rates for a $^3(\text{CH}_3\text{C(O)CH}_2\text{O})_{\cdots}\text{CH}_3\text{C(O)CH}_2\text{O}$ conformer with a large distance between radical centers.
Extra slide 5: Energy levels and rates for a $^3(\text{CH}_3\text{C(O)}\text{CH}_2\text{O}...\text{CH}_3\text{C(O)}\text{CH}_2\text{O})$ conformer with a small distance between radical centers.