Evaluating mechanisms for dimer formation from RO₂ + RO₂ reactions

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RO₂ + RO₂ observed to form ROOR dimers – but how?

- Two well-known channels for gas-phase RO₂ + RO₂:

 RO + RO + O₂
 R=O + ROH + O₂

 Also 3) ROOR + O₂, but little evidence in gas phase for small R.
- For larger R (≥ 3 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. monoterpene autoxidation, as they are the genuine "**ELVOC**".
- Molecular-level RO₂ + RO₂ mechanism remains a mystery, and a "challenge for computational methods" (Dibble 2008).
- RO₂ + RO₂ generally believed (since 1957) to proceed via a RO₄R tetroxide intermediate, but what then?

Russell mechanism



• Russell (1957): different $RO_2 + RO_2$ channels correspond to different geometries and/or decomposition pathways of RO_4R .



- Computational studies using DFT geometries do find multiple RO₄R 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 RO₄R decomposition.



This TS not found in other/earlier studies

Lee *et al* (PCCP 2016) proposed mechanism (*DFT* + *CCSD*(*T*) + *tricks*)

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- RO + RO yield determined by RO...RO binding, carbonyl + ROH yield controlled by the bimolecular₁₀ 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 \Rightarrow RO₄R reaction \approx -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.

 $R = CH_3$, CH_3CH_2 , $(CH_3)_2CH$, $(CH_3)_3C$, BuOH, $CH_3C(O)CH_2$, $BuONO_2$

- Ordering qualitatively agrees with expts, e.g. higher barrier for t-but RO₂
- Agrees with Ghigo (2003) on CH₃O₄CH₃ decomposition.

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S_{decomp}

RO₂

 $+ RO_2$

 $\mathsf{TS}_{\mathsf{form}}$

Rate-limiting step may be RO₄R **formation** not decomposition

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- O₂ in RO...O₂...RO very weakly bound: we model subsequent reactions with RO...RO.
- ³(CH₃O...CH₃O) weakly bound with respect to CH₃O + CH₃O;
 ~5 kcal/mol according to both CCSD(T)//DFT and XMC-QDPT2.
- ³(RO...RO) binding increases with complexity of R, but surprisingly slowly (intramolecular 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(CH₃O...CH₃O)

- 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 T₁ and S₁ are small; 0.3 and 25 cm⁻¹, respectively. This gives an **ISC** rate of about 10⁸ 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).



ISC rate for larger ³(RO...RO)

- Larger ³(CH₃O...CH₃O) have multiple conformers. Our main test system: ³(CH₃C(O)CH₂O...CH₃C(O)CH₂O).
 - Smallest system for which ROOR formation unambiguously observed (Berndt *et al.*, 2018)



- ISC between T₁ and S₁ varies enormously between conformers: from 1 to 10⁹ s⁻¹ (depending on distance between radical centers)
- ISC between T_1 and S_2/S_3 varies less, always around 10⁸ s⁻¹.



ISC rates roughly around 10^8 s^{-1} found also for large ³(RO...RO) from *e.g.* alpha-pinene + O₃ and trimethylbenzene + OH (also 1-butene + OH)



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Note: arbitrary conformers, no sampling (yet)

Conclusion: ROOR probably forms by intersystem crossing

- Ghigo/Lee mechanism for ROOR formation from $RO_2 + RO_2$ seems promising, with a few modifications:
 - Entrance-channel barrier exists, and might be rate-limiting
 - Barriers for RO_4R formation and decomposition are probably all well below $RO_2 + RO_2$ in E_{elec} .
- ISC rates for ³(RO...RO) likely to be at least 10⁸ s⁻¹, and involve not only T₁ and S₁ but also S₂, S₃ states.
- Fragmentation and H-shift channels of ³(RO...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 MeO₄Me

(similar orbitals picked for all other RO_4R)





Extra slide 2: CASSCF(10,8) orbitals for ³(CH₃O....CH₃O)





Note: the fact that a 10-electron, 8-orbital active space is appropriate for describing both the formation/decomposition of RO_4R 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(CH₃C(O)CH₂O...CH₃C(O)CH₂O)



similar orbitals picked for all other ³(RO...OR)



Extra slide 4: Energy levels and rates for a ³(CH₃C(O)CH₂O...CH₃C(O)CH₂O) conformer with a large distance between radical centers





Extra slide 5: Energy levels and rates for a ³(CH₃C(O)CH₂O...CH₃C(O)CH₂O) conformer with a small distance between radical centers

