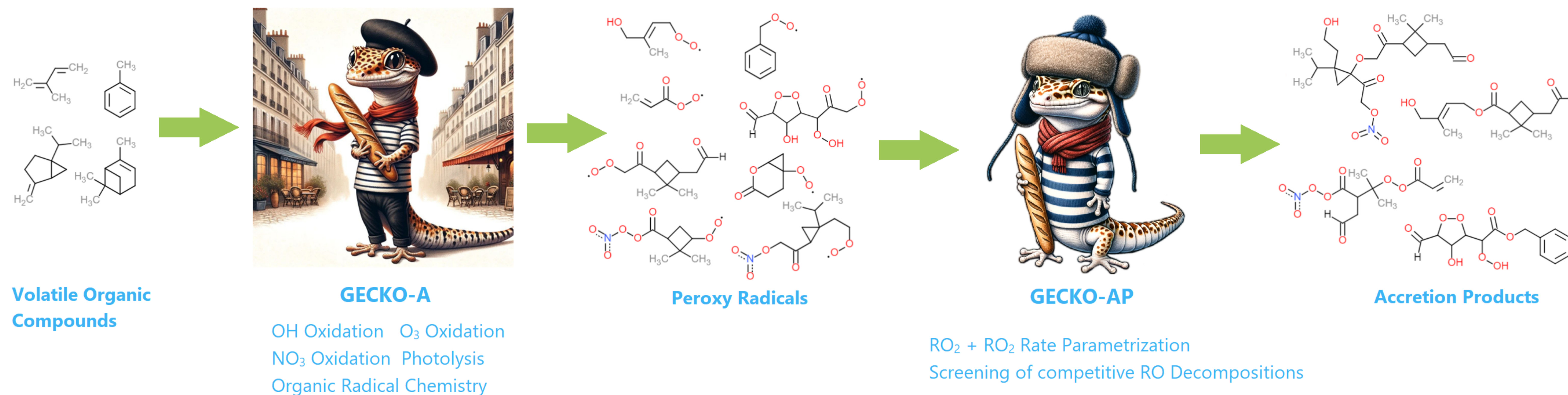




ETHER AND ESTER FORMATION FROM PEROXY RADICAL RECOMBINATION

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INTRODUCTION: ETHERS AND ESTERS? HOW?

The least volatile organic compounds formed in-situ in the atmosphere are likely accretion products from recombination reactions of peroxy radicals (RO₂). It has long been assumed that the only possible accretion product channel in this reaction is that forming a peroxide (RO₂ + RO₂ → ROOR + O₂), but in our previous experimental work [1] we discovered that a rapid alkoxy radical (RO) decomposition may occur in the intermediate (RO...OR) complex, preceding the accretion step and forming a fragmented but more stable ester product. This raises the question of which other RO₂ + RO₂ reactions could result in products like these. We explored this question using a modified version of the GECKO-A [2] software, in which product branching ratios were estimated for 301 055 RO₂ pairs from a set of 10 971 RO₂ generated by GECKO-A from the following set of atmospheric precursor molecules: **n-Decane, Toluene, Isoprene, α-pinene, β-pinene, Limonene, β-Ocimene, Sabinene, Δ-3-Carene, Myrcene, and β-Caryophyllene.**

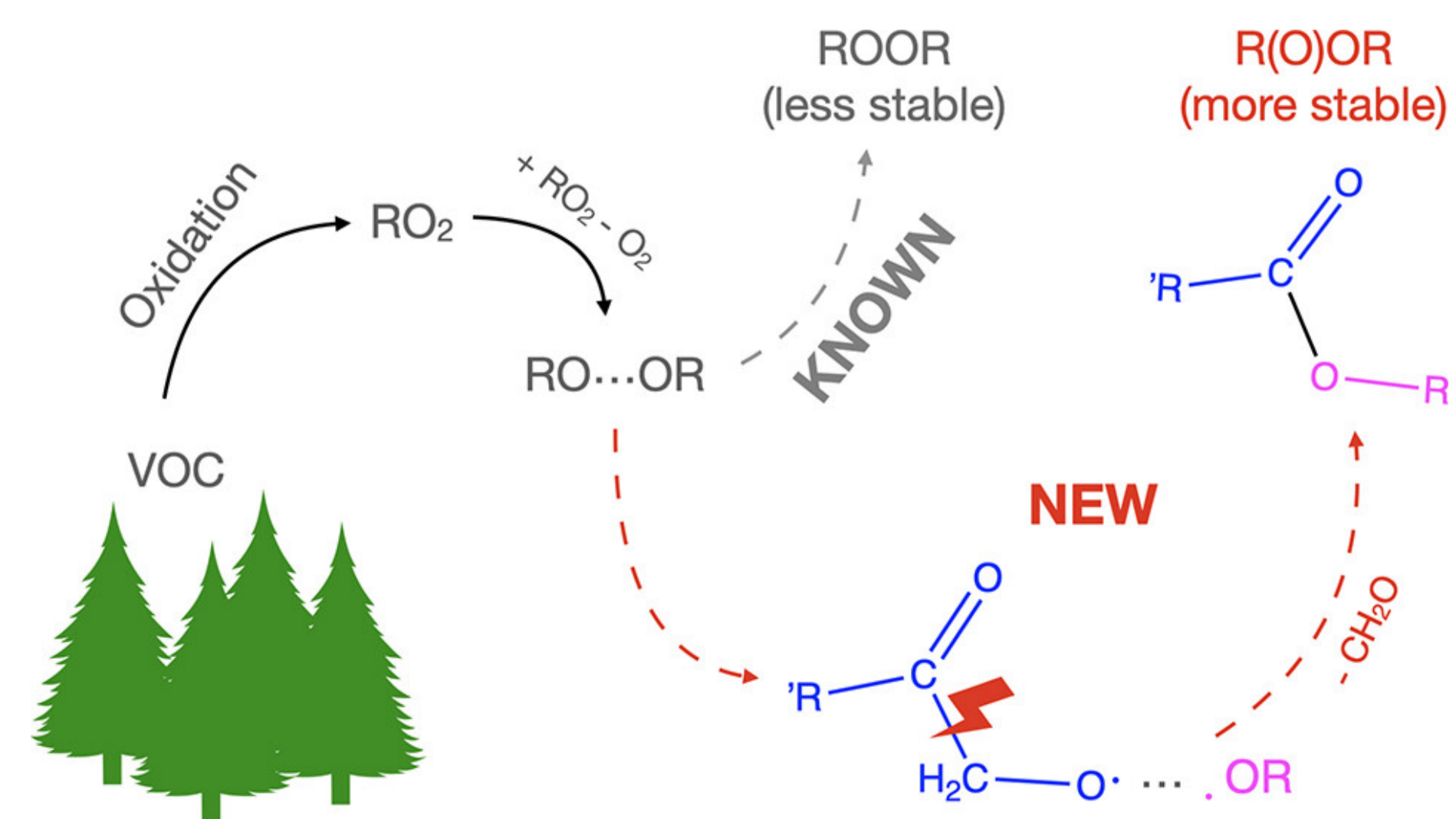
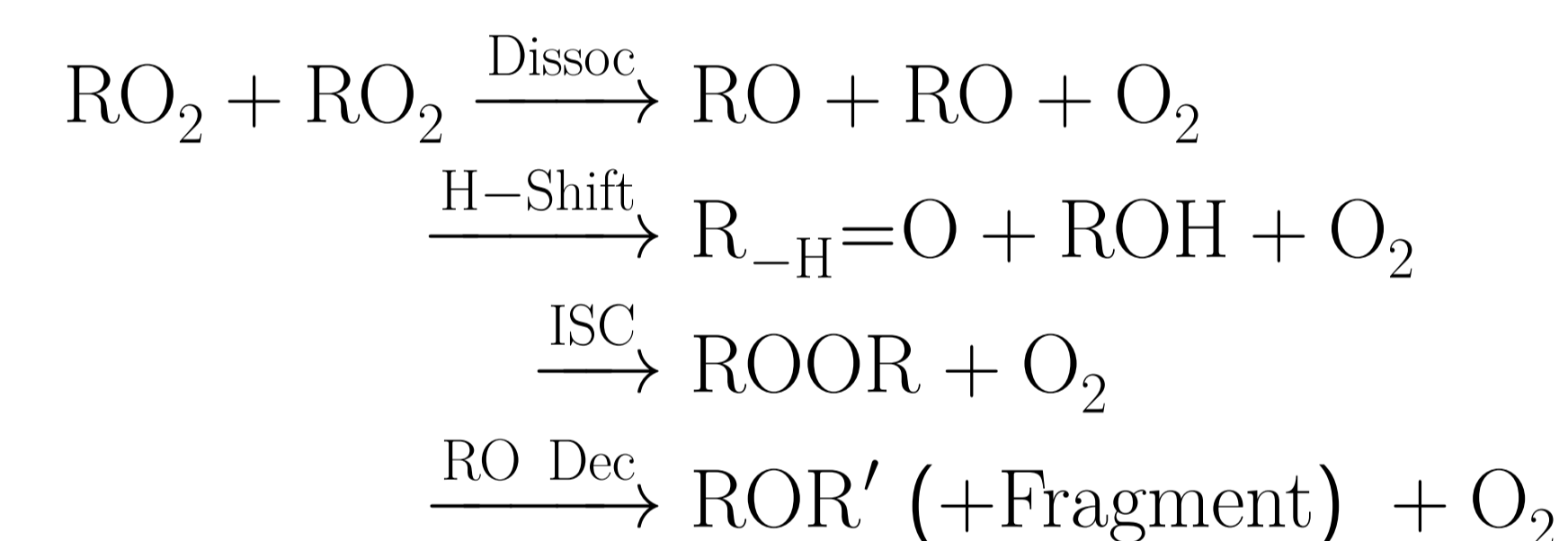


Figure 1: Schematic on ester formation for RO₂ recombination. Originally from [1]

METHODS: THE GECKO-AP CODE

With our new RO channel, the known products of RO₂ + RO₂ are:



Based on known rates for the Dissoc, H-shift and ISC channels, [3] it was assumed that the RO decomposition becomes competitive around $k_{\text{RODec}} \approx 10^9 \text{ s}^{-1}$. Competing RO unimolecular reactions were searched using Vereecken's SAR models for RO β-scission [4] and unimolecular H-shift [5], and the ether/ester accretion products corresponding to each RO reaction (as well as the ROOR product) were generated by the code. Due to the combinatorial amount of potential products, **RO₂ pairs** were filtered out based on RO₂ yields and recombination rates:

$$\frac{k_{\text{RO}_2\text{RO}_2, \alpha+\beta}}{5.3 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}} y_\alpha y_\beta < 0.003$$

where y_α and y_β are the yields of the two RO₂. Reaction channels were filtered based on competitiveness:

$$\frac{k_{\text{RODec}}}{10^9 \text{ s}^{-1} + \sum_i^{n_\alpha} k_i + \sum_j^{n_\beta} k_j} < 0.05$$

The resulting set of RO₂ + RO₂ products was analysed in order to learn about the reactivity trends and atmospheric implications of this new reaction channel.

CONCLUSIONS: NEW INSIGHTS ON RO₂ + RO₂

Reaction channel trends

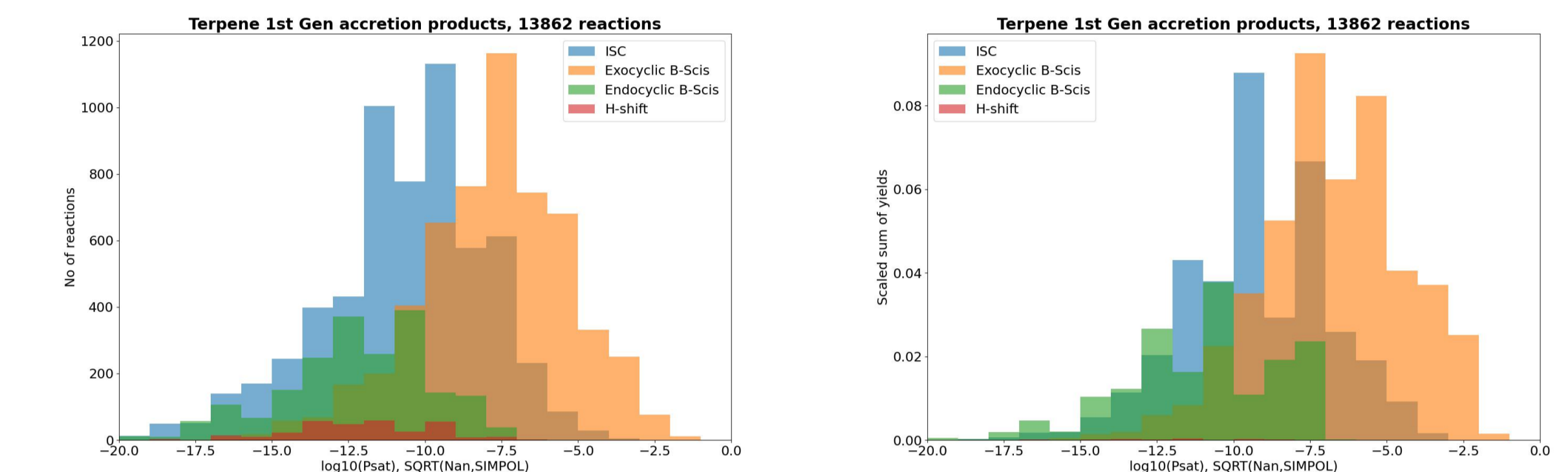


Figure 2: p_{Sat} histograms (in atm) for the 1st Gen products from the Terpene molecules, scaled by yield on the right. **Endocyclic β-scission** products have low p_{Sat} and high yields. **Exocyclic β-scission** products have higher p_{Sat} , and **Unimolecular H-shift** products have low volatilities but low yields.

Precursor molecule trends

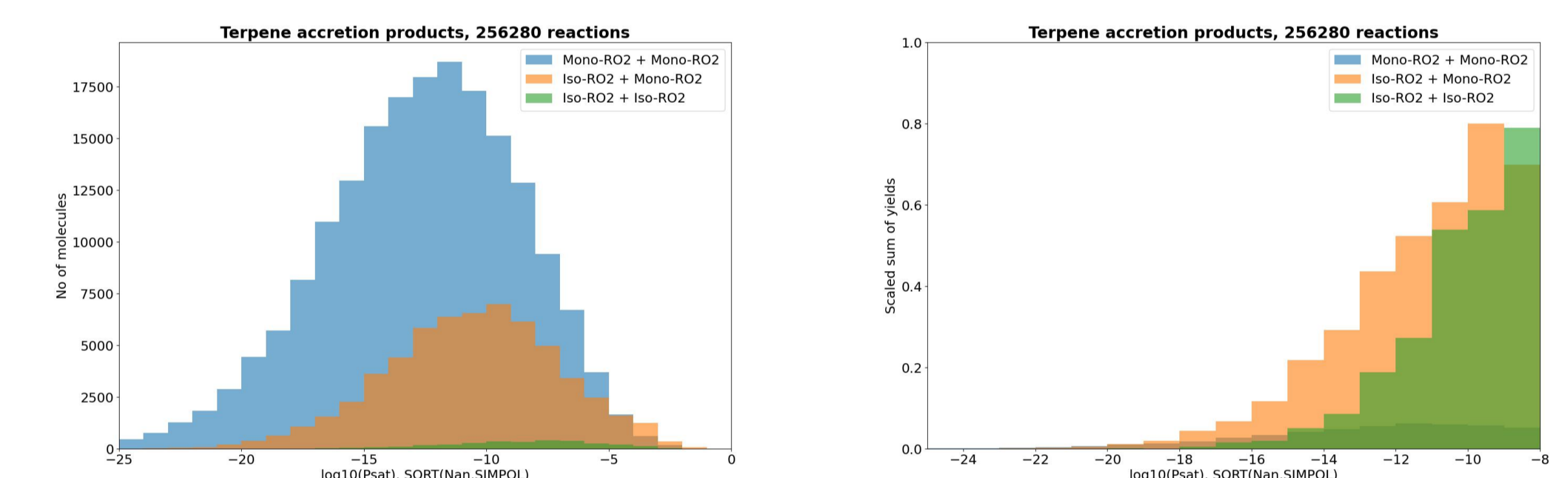
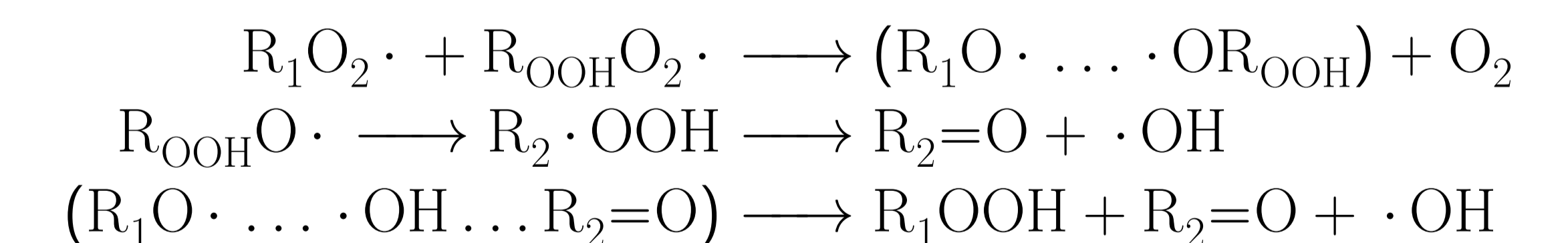


Figure 3: p_{Sat} histograms (in atm) for the Terpene accretion products, scaled by yield AND Isoprene/Monoterpene emission rates on the right. It seems that Isoprene-RO₂ + Monoterpene-RO₂ products contribute greatly to particle growth.

Accretion product inhibiting reactions All RO₂ + RO₂ reactions of highly oxidized radicals do not lead to accretion product formation, unlike what has been previously assumed. [3] This is due to RO decompositions forming small inorganic radicals. This is especially common when the RO₂ have multiple -OOH groups!



REFERENCES

- O. J. Peräkylä, T. Berndt, L. Franzon, G. Hasan, M. Meder, R. Valiev, C. Daub, J. G. Varelas, F. M. Geiger, R. J. Thomson, M. P. Rissanen, T. Kurtén and M. K. Ehn, *J. Am. Chem. Soc.*, 2023, **145**, 7780-7790
- B. Aumont, S. Szopa, and S. Madronich, *Atmos. Chem. Phys.*, 2005, **5**, 2497-2517
- G. Hasan, PhD thesis, University of Helsinki, 2023
- L. Vereecken and J. Peeters, *Phys. Chem. Chem. Phys.*, 2009, **11**, 9062-9074
- L. Vereecken and J. Peeters, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12608-12620

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