Interactive comment on “H-migration in peroxy radicals under atmospheric conditions” by Luc Vereecken and Barbara Nozière

Anonymous Referee #1

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This paper reports the structure-activity relationship (SAR) for the rate coefficients for the isomerization reactions of organic peroxy radicals (RO2) to QOOH based on the experimental and theoretical investigations. It adds new class of knowledge on the atmospheric chemistry. I request the authors to address the following comment on the assumption in the analysis of experiments.

[1] In the analysis of experimental data, authors simple one-way reaction (R1). RO2 \(\rightarrow\) HOOQO2 (R1) However, this should be actually the two-step reactions. RO2 \(\rightarrow\) QOOH (R2) QOOH \(\rightarrow\) RO2 (R-2) QOOH + O2 \(\rightarrow\) HOOQO2 (R3) The assumption of simple one-way reaction (R1) is only valid when \(k_3[O2] \gg k_{-2}\). My rough calculation shows that \(k_{-2}\) may be as large as \(10^7\) to \(10^8\) s\(^{-1}\), which is comparable order with \(k_3[O2]\) at the authors experimental condition, (0.9 atm, 298 K, synthetic air), \(k_3[O3] = 3 \times 10^7 \sim 1 \times 10^8\). Authors should properly discuss the effects of the backward reactions (R-2).