

An in-depth answer to the comment by Referee #1 required a sizable addition to the manuscript, so we already provide a version of this addition at this time, in case any of the referees would like to comment before we submit our full revised version. The text below may still be changed somewhat to allow better integration in the text.

Comment by Referee #1:

In the analysis of experimental data, authors simple one-way reaction (R1). $RO_2 \rightarrow HOOQO_2$ (R1) However, this should be actually the two-step reactions. $RO_2 \rightarrow QOOH$ (R2) $QOOH \rightarrow RO_2$ (R-2) $QOOH + O_2 \rightarrow HOOQO_2$ (R3) The assumption of simple one-way reaction (R1) is only valid when $k_3[O_2] \gg k_{-2}$. My rough calculation shows that k_{-2} may be as large as 10^7 to 10^8 s⁻¹, which is comparable order with $k_3[O_2]$ at the authors experimental condition, (0.9 atm, 298 K, synthetic air), $k_3[O_2] = 3 \times 10^7 \sim 1 \times 10^8$. Authors should properly discuss the effects of the backward reactions (R-2)

Answer:

The reversibility of the reaction is certainly an interesting aspect of the chemistry. We have collected our thoughts in a new section we propose to include in the paper, where we find that the available data suggests that reverse H-migration is not expected to be a dominant path for the alkyl radical products. Although we were aware that the H-migration (R1) could be somewhat reversible, the experimental analysis only takes reaction (R1) into account as a simplification for the three reactions (R1)-(R-2)-(R3). The rate coefficient measured experimentally, k_{iso} , is the effective rate coefficient for product formation, as governed by the competition between R-2 and R3, i.e. we only observe the overall phenomenological rate coefficient. The reverse reaction (R-2) appears to be significantly slower than (R3) by an order of magnitude or more, and certainly can not be a dominant path, otherwise the net isomerization could not have been observed experimentally, and could not have had the same good agreement with the theoretical data. As (R3) is much faster than (R1), the later was the kinetically limiting step in the reaction system (R1)-(R-2)-(R3), and the effective rate for product formation was reported as the rate of H-migration. The text will be changed at the appropriate places to reflect this simplification, referring to the new section below.

New section: The fate of the radical products

In atmospheric chemistry, the unimolecular reactions of an alkyl radical are typically not considered explicitly. Mechanisms such as the Master Chemical Mechanism assume, by default, O_2 addition for all alkyl radicals (Jenkin et al., 1997), unless a special reaction is known to occur; examples of the latter include $>C^*(OH) + O_2$, epoxide formation in C^*-COOH , or OH elimination in C^*OOH . For aliphatic alkyl radicals, the rate of H-migration or elimination reactions rarely reaches 10^4 s⁻¹ at room temperature, such that O_2 addition is dominant (Miyoshi, 2011; Villano et al., 2011; Wang et al., 2015). The weaker OO–H bond in hydroperoxides, however, facilitates H-migration in *QOOH radicals, reversing the RO_2 H-migration. If we assume that only the reverse *QOOH to RO_2 reaction can occur in competition with O_2 addition, the effective rate of $HOOQO_2$ formation will be dependent on the rate of *QOOH formation, k_1 , and of the reverse reaction k_{-1} competing against the O_2 addition on the alkyl radical site, $k_{O_2}[O_2]$:

$$k_{eff}(T) = k_1(T) \frac{k_{-1}(T)}{k_{-1}(T) + k_{O_2}(T)[O_2]}$$

i.e. the faster the reverse reaction, the slower effective product formation k_{eff} will be for a given $k_{O_2}[O_2]$ value. A structure activity relationship for RO₂ H-migration should not account for the effect of the reverse H-migration reaction, as other reaction paths may be accessible, such as alkyl ring closure reactions, epoxidation, HO₂ elimination forming alkenes, and other rearrangements which have been amply studied at higher temperatures for combustion systems (see e.g. Miyoshi, 2011). A full analysis of the fate of the [•]QOOH intermediates is outside the scope of the present paper, and we refer to the cited papers for reaction rate rules.

The experimental studies by Nozière and Vereecken (2019) examined migration of aliphatic H-atoms, which are comparatively slow, have a high forward barrier, and are endoergic by ~ 15 kcal mol⁻¹, leading to reverse barriers of 10 kcal mol⁻¹ or less. The reverse [•]QOOH H-migration concomitantly has a rather high rate coefficient k_{-1} , and is thus potentially affecting k_{eff} . A theory-based comparison by Miyoshi (2011) found that for 1,7-H-shift spans or larger, the entropic disadvantage of the cyclic H-migration TS against the more facile O₂ addition (0.2 atm O₂) allows the latter to dominate at room temperature by a factor $\sim 10^3$ or higher. For 1,5 to 1,6-H-migrations, however, the ratio $k_{-1}(298K)/k_{O_2}(298K)[O_2]$ is closer to 10, indicating that the effective rate of product formation $k_{eff}(298K)$ could be reduced by $\sim 10\%$ compared to the elementary reaction rate for RO₂ H-migration. Since 1,5- and 1,6-H-migrations are typically the most favorable H-migration spans, this reverse reaction may need to be taken into account for highly accurate analyses. Future work could examine this aspect in more detail. At the present time, the estimated impact is smaller than the total uncertainties on the measurements (Nozière and Vereecken, 2019); experiments at elevated O₂ concentrations could directly probe the impact on the phenomenological rate coefficient. The fact that the H-migration rate was observable in those reaction conditions (0.9 atm synthetic air), and the good agreement between theory and experiment in those studies, precludes a reverse reaction that is dominant over O₂ addition.

The RO₂ H-migration reaction rates are subject to Bell-Evans-Polanyi relationships, where more exothermic reactions have lower forward energy barriers and higher reverse barriers. A good correlation is only found within a single substituent group though, as e.g. allyl/vinoxy resonance stabilization or H-bonding can affect the post-TS stabilization of the product by a larger amount as in the transition state. Faster H-migration reactions then tend to have slower reverse reactions, and RO₂ reactions fast enough to be important in atmospheric conditions are likely to have reverse reactions slow enough to safely assume that O₂ addition in the product alkyl radical is dominant. The experiments by Nozière and Vereecken (2019) then appear to be a worst case scenario for atmospheric chemistry regarding the difference between elementary and phenomenological rates, and we propose that reverse alkyl H-migration generally has a very limited impact under atmospheric conditions. For some radicals, such as allyl-stabilized or aromatic radicals, effective O₂ addition is significantly slower than for aliphatic alkyl radicals (Peeters et al., 2009; Vereecken, 2019). Furthermore, such resonance stabilized radicals are readily formed, with the SAR described in this paper showing that unsaturated functionalities generally lead to fast RO₂ migration of the β -H-atoms. The same electronic stabilization that hampers O₂ addition, however, also reduces the rate of the reverse alkyl radical H-migration, mitigating the slower HOOQOO[•] formation. Unsaturated alkyl radicals also allows for alkyl cyclisation reactions; the predicted rate coefficients near room temperature are of the order of 10⁶ s⁻¹ or less, and are not competitive against O₂ addition (Wang et al., 2015).

For non-alkyl radical products, reversal of the reaction may be more important. For oxygen-based product radicals this has been discussed in detail, see the sections on hydroxy-, hydroperoxy-, carboxylic H-migration.

References

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