Structure-activity relationships for unimolecular reactions of peroxy radicals, RO₂, at atmospheric temperatures

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The oxidation of most organic matter in the atmosphere proceeds through a peroxy radical stage, ROO•, which typically react with NO, HO₂ or other RO₂ compounds. Recently, unimolecular reactions of RO₂ radicals have also been recognized as important reaction channels. We describe a structure-activity relationship (SAR) for H-migration in (substituted) RO₂ radicals, and for ring closure reactions in unsaturated RO₂ radicals.

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Introduction

The oxidation of most volatile organic compounds (VOCs) emitted to the atmosphere proceeds by radical reaction steps, where peroxy radicals, ROO•, are critical intermediates formed by addition of O₂ molecules to carbon-based radicals. The chemistry of these RO₂ radicals in high-NOx conditions is well-known, forming alkoxy radicals, RO•, and NO₂. In low-NOx and pristine conditions, the RO₂ radicals react with HO₂ and other R'O₂ radicals, but can have a sufficiently long lifetime to also undergo unimolecular reactions.

Hydrogen atom migration, forming a hydroperoxide (-OOH) and a new peroxy radical site after addition of an additional O₂ on the newly formed radical site, has been studied extensively in some compounds, such as isoprene where it was shown to be the critical step in OH radical regeneration (Peeters et al. 2009, 2014), or in the formation of highly oxidized molecules (HOMs).

RO₂ ring closure reactions have likewise been studied, where e.g. for β-pinene it has been shown to be a critical step governing the yield of the decomposition products such as acetone and nopinone (Kaminsky et al. 2017; Vereecken and Peeters, 2004, 2012).

Unimolecular reactions of RO₂ are known to form or regenerate more reactive OH and HO₂ radicals. They also allow for auto-oxidation of VOCs by a series of sequential rearrangement + O₂ addition events, leading to highly-oxygenated, low-volatility compounds that affect aerosol
formation and growth, and can affect air quality and climate change. As pollution levels drop, the reduced impact of NOx scavenging of RO2 enables these unimolecular reactions to become more prominent even outside pristine environments.

Despite the interest in RO2 unimolecular reactions, and the potential impact on atmospheric chemistry, no widely applicable structure-activity relationships (SARs) have hitherto been proposed to allow systematic incorporation of such unimolecular reactions in gas phase atmospheric kinetic models. Theory-based work has recently enabled the formulation of an extensive SAR for H-migration, and is currently available as a discussion paper in Atmospheric Chemistry and Physics Discussions (Vereecken and Nozière, 2020). We also report results of ongoing SAR development for ring closure in unsaturated RO2.

### H-migration SAR derivation

The training data set consists mostly of a series of theoretical predictions:

- Quantum chemical characterizations of reactant and transition states:
  - CCSD(T)/aug-cc-pVTZ // M06-2X/aug-cc-pVTZ
  - CBS-QB3 // B3LYP/6-31G(d,p)
  - CCSD(T) // M05-2X/6-311G(d,p)
  - B3LYP/6-31G(d,p) // B3LYP/6-31G(d,p)

- Theoretical kinetic calculations:
  - Full multi-conformers transition state theory (MC-TST)
  - Relative multi-conformers transition state theory (rel-MC-TST)

This data set is enhanced by data from a set of extensive studies available in the literature: Finally, a set of experimental measurements of rate coefficient for H-migration described in the literature are used as training or validation data sets.

The RO2 H-migration reactivity trends for the following reaction classes are considered:

- 1,4 up to 1,9 H-migration spans
- Migration of H-atoms bonded as : C–H, O–H, OO–H, C(=O)O–H
- α-substitutions : –R, –OH, –ONO₂, =O, –OR
- β-substitutions : C–OH, C=O, C=C
- Substitutions near the –OO• radical site or the migrating H site

Temperature range : 200-450 K
Pressure range : high pressure (no pressure effect is expected in atmospheric conditions)
H-migration SAR structure

From the above data, the rate coefficients for H-migrations are calculated and tabulated in lookup tables, ordered per migration span, –OO site substituents, and migrating-H site substituents. If multiple data points are available for a particular combination of SAR parameters, the data is geometrically averaged. For SAR parameter combinations where no direct data is available, the reactivity trend is estimated relative to aliphatic RO₂ substitution patterns. For parameter combinations where data is available only near room temperature, the temperature dependence across the entire T-range is transferred from similar SAR classes. Table 1 gives an example of a lookup table in unsaturated RO₂, where typically high rate coefficients are predicted. For some reaction classes, the data is scarce, and a formula is preferred, which uses a reference rate coefficient from another table, corrected by a temperature-dependent factor. A full set of tables and correction factors can be found in Vereecken and Nozière (2020).

H-migration SAR performance

The theoretical data on mono-substituted RO₂ constitutes the training data set of the SAR and their comparison against the SAR thus only provides goodness-of-fit metrics that are of less importance. Below, comparisons against more relevant experimental and theoretical data are show.

For the available experimental data, typically multi-functionalized RO₂, and occasionally outside the temperature range covered by the SAR, the SAR reproduces the measured rate coefficient on average within a factor of two (shown as dotted lines parallel to 1:1 diagonal). Only one significant outlier is found, and the corresponding SAR class was found to be based on the least reliable theoretical data, suggestion further improvements should be readily accessible.

For a validation set consisting of theoretical data for multi-functionalized species, most of the predictions were found to be within a factor 10 (shown as dashed lines parallel to 1:1 diagonal) of the SAR predictions.
**H-migration SAR summary**

The validation indicate that the SAR should be sufficiently accurate for many atmospheric modeling applications. The SAR also provides a valuable framework for future improvements, based on both experimental and theoretical data.

The fastest H-migrations are typically found for 1,5 and 1,6 H-migrations. Aldehyde functionalities, or double bonds allowing the formation of allylic product radicals greatly enhance the reaction rates, and lead to the highest predicted rate coefficients exceeding 1 s\(^{-1}\).

**Ring closure SAR**

The current data set for RO\(_2\) ring closure encompasses 4-membered to 7-membered ring formation, with ring closure on both the inside and the outside double bonded carbon.

As expected, formation of 4-membered rings or smaller is found to have large energy barriers exceeding 30 kcal mol\(^{-1}\), and is not competitive in atmospheric conditions. The most energetically favorable ring closures are 5- and 6-membered rings, whereas 7-membered or larger rings become somewhat less favorable both energetically and entropically.

For 5/6-membered rings, the main reactivity trends can be summarized as follows:
- Formation of an exo-cyclic radical site is more favorable than an endo-cyclic radical site
- Alkyl substitution on the COO\(^*\) carbon has very little influence, contrary to H-migration
- Each alkyl substituent on the –CH=CH\(_2\) group reduces the barrier by about 1.5 kcal mol\(^{-1}\)
- The reaction rates at 298K ranges from 10\(^{-2}\) to 10\(^{3}\) s\(^{-1}\)
- The reactions are about thermoneutral

The rate coefficients are comparable to, or exceeding, those of H-migration in many cases, suggesting that ring closure in unsaturated RO\(_2\) can likewise be competitive in pristine or mildly polluted atmosphere. The product radical formed will rapidly react with O\(_2\), forming a cycloperoxide-peroxy radical; at room temperature the reverse ring opening is not expected to be competitive.

**General conclusions**

As long as the co-reactant concentrations of HO\(_2\)/RO\(_2\)/NO for RO\(_2\) bimolecular reactions are not overly high, both H-migration and ring closure reactions are viable pathways in the oxidation of VOCs in the atmosphere. The presence of multiple double bonds in most of the non-methane VOCs emitted (isoprene, monoterpenes,...) enhances the autoxidation rate significantly. These reaction channels can thus influence the formation of highly oxygenated molecules and aerosols, as well as OH and HO\(_2\) radicals, with repercussions for the oxidative capacity of the atmosphere, air quality, and climate change.
References


Table 1: Rate coefficients for allylic H-migration in peroxy radicals with a double bond outside the TS ring, accounting for all abstractable H-atoms in the group. See Vereecken and Nozière (2020) for lookup tables for other substitution patterns.

\[
\begin{align*}
\text{Substitution pattern} & \quad k(298 \text{ K}) / \text{s}^{-1} & \quad A / \text{s}^{-1} & \quad n & \quad E_a / \text{K} \\
\text{H-atom} & \quad -\text{OO}^* & & & \\
\text{1,4-H-migration} & & & & \\
\text{=C–CH}_2 & \quad \text{–CH}_2\text{OO}^* & \quad 1.56\times10^4 & 9.82E+01 & 2.65 & 9172 \\
& >\text{CHOO}^* & \quad 7.72\times10^6 & 9.82E+01 & 2.65 & 9382 \\
& >\text{C(OO)}^* & \quad 2.55\times10^5 & 9.82E+01 & 2.65 & 9026 \\
\text{=C–CH}_2 & \quad \text{–CH}_2\text{OO}^* & \quad 9.52\times10^5 & 9.82E+01 & 2.65 & 8634 \\
& >\text{CHOO}^* & \quad 7.50\times10^4 & 9.82E+01 & 2.65 & 8019 \\
& >\text{C(OO)}^* & \quad 8.66\times10^3 & 9.82E+01 & 2.65 & 7290 \\
\text{1,5-H-migration} & & & & \\
\text{=C–CH}_2 & \quad \text{–CH}_2\text{OO}^* & \quad 2.71\times10^4 & 5.52E-47 & 18.56 & -525 \\
& >\text{CHOO}^* & \quad 2.58\times10^2 & 6.10E-25 & 11.23 & 3540 \\
& >\text{C(OO)}^* & \quad 4.60\times10^5 & 6.74E-03 & 3.9 & 8104 \\
\text{=C–CH}_2 & \quad \text{–CH}_2\text{OO}^* & \quad 6.15\times10^4 & 6.10E-25 & 11.23 & 2595 \\
& >\text{CHOO}^* & \quad 1.87\times10^9 & 6.10E-25 & 11.23 & 2263 \\
& >\text{C(OO)}^* & \quad 1.30\times10^2 & 6.10E-25 & 11.23 & 3744 \\
\text{1,6-H-migration} & & & & \\
\text{=C–CH}_2 & \quad \text{–CH}_2\text{OO}^* & \quad 2.04\times10^7 & 8.49E-55 & 20.84 & -1928 \\
& >\text{CHOO}^* & \quad 7.68\times10^2 & 7.71E-37 & 15.05 & 1531 \\
& >\text{C(OO)}^* & \quad 4.27\times10^6 & 7.72E-46 & 17.86 & -1061 \\
\text{=C–CH}_2 & \quad \text{–CH}_2\text{OO}^* & \quad 7.39\times10^4 & 7.71E-37 & 15.05 & 857 \\
& >\text{CHOO}^* & \quad 6.69\times10^9 & 7.71E-37 & 15.05 & 200 \\
& >\text{C(OO)}^* & \quad 4.17\times10^4 & 6.99E-10 & 6.43 & 6275 \\
\text{1,7-H-migration} & & & & \\
\text{=C–CH}_2 & \quad \text{–CH}_2\text{OO}^* & \quad 8.22\times10^7 & 4.62E-48 & 18.62 & -1503 \\
& >\text{CHOO}^* & \quad 2.55\times10^2 & 4.62E-48 & 18.62 & 219 \\
& >\text{C(OO)}^* & \quad 5.72\times10^3 & 4.62E-48 & 18.62 & 665 \\
\text{=C–CH}_2 & \quad \text{–CH}_2\text{OO}^* & \quad 3.56\times10^4 & 4.62E-48 & 18.62 & -568 \\
& >\text{CHOO}^* & \quad 2.27\times10^9 & 4.62E-48 & 18.62 & -1120 \\
& >\text{C(OO)}^* & \quad 4.30\times10^4 & 4.62E-48 & 18.62 & -624 \\
\end{align*}
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\(a\) Averaged temperature-dependence from other reactions used

\(b\) \(k(298 \text{ K})\) anchor value derived from relative rates of aliphatic RO\(_2\), scaled to unsaturated RO\(_2\)