

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

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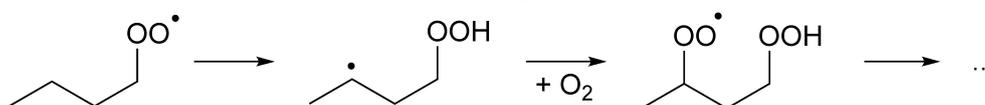
The oxidation of most organic matter in the atmosphere proceeds through a peroxy radical stage, ROO[•], which typically react with NO, HO₂ or other RO₂ compounds. Recently, unimolecular reactions of RO₂ radicals have also been recognized as important reaction channels. We describe a structure-activity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

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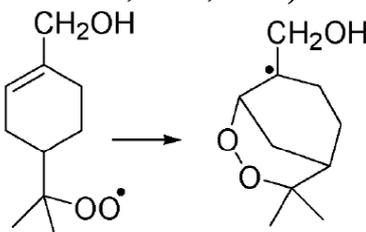
Introduction

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-NO_x conditions is well-known, forming alkoxy radicals, RO[•], and NO₂. In low-NO_x 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 a 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 NO_x scavenging of RO_2 enables these unimolecular reactions to become more prominent even outside pristine environments.

Despite the interest in RO_2 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 RO_2 .

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 RO_2 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

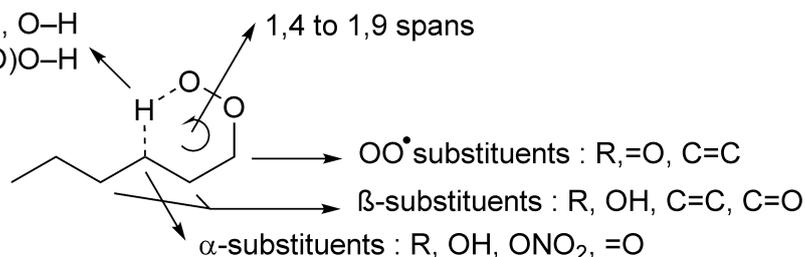
α -substitutions : -R, -OH, -ONO₂, =O, -OR

β -substitutions : C-OH, C=O, C=C

Substitutions near the -OO[•] radical site or the migrating H site

H-type : C-H, O-H

OO-H, C(=O)O-H



Temperature range : 200-450 K

Pressure range : high pressure (no pressure effect is expected in atmospheric conditions)

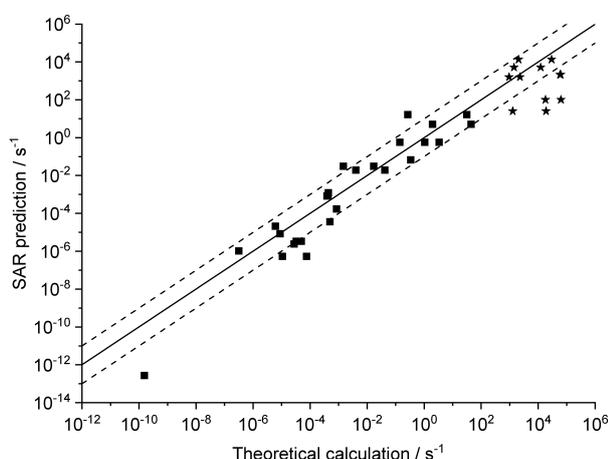
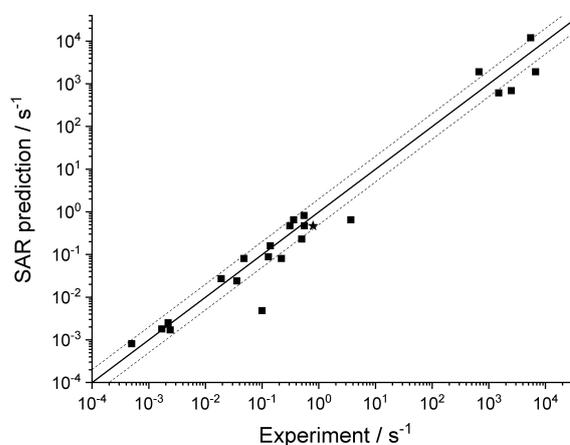
H-migration SAR structure

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 RO_2 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 RO_2 , 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 RO_2 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 shown.

For the available experimental data, typically multi-functionalized RO_2 , 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.

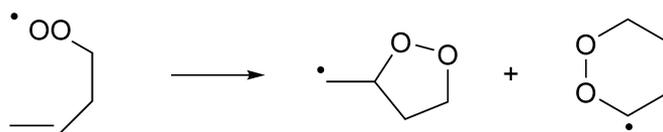
H-migration SAR summary

The validation indicates 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

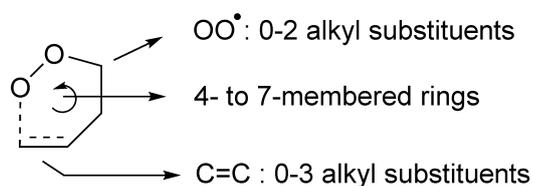
The current data set for RO_2 ring closure encompasses 4-membered to 7-membered ring formation, with ring closure on both the inside and the outside double bonded carbon.



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^\bullet carbon has very little influence, contrary to H-migration
- Each alkyl substituent on the $-\text{CH}=\text{CH}_2$ group reduces the barrier by about $1.5 \text{ kcal mol}^{-1}$
- 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.

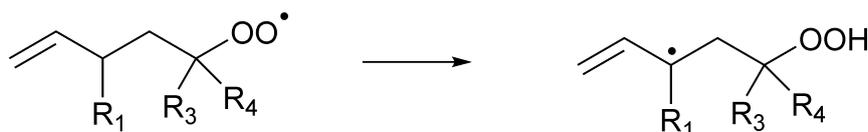
General conclusions

As long as the co-reactant concentrations of $\text{HO}_2/\text{RO}_2/\text{NO}$ 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

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Table 1: Example lookup table from the SAR, predicting 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.



Substitution pattern		$k(298\text{ K}) / \text{s}^{-1}$	$k(200\text{-}450\text{K}) = A \times (T/\text{K})^n \times \exp(-E_a / T)$		
H-atom	$-\text{OO}^\bullet$		A / s^{-1}	n	E_a / K
1,4-H-migration					
$=\text{C}-\text{CH}_2-$	$-\text{CH}_2\text{OO}^\bullet$	1.56×10^{-5}	$9.82\text{E}+01$	2.65	9172
	$>\text{CHOO}^\bullet$ ^{a,b}	7.72×10^{-6}	$9.82\text{E}+01$	2.65	9382
	$>\text{C}(\text{OO}^\bullet)-$ ^{a,b}	2.55×10^{-5}	$9.82\text{E}+01$	2.65	9026
$=\text{C}-\text{CH}<$	$-\text{CH}_2\text{OO}^\bullet$ ^a	9.52×10^{-5}	$9.82\text{E}+01$	2.65	8634
	$>\text{CHOO}^\bullet$ ^{a,b}	7.50×10^{-4}	$9.82\text{E}+01$	2.65	8019
	$>\text{C}(\text{OO}^\bullet)-$ ^{a,b}	8.66×10^{-3}	$9.82\text{E}+01$	2.65	7290
1,5-H-migration					
$=\text{C}-\text{CH}_2-$	$-\text{CH}_2\text{OO}^\bullet$	2.71×10^0	$5.52\text{E}-47$	18.56	-525
	$>\text{CHOO}^\bullet$ ^{a,b}	2.58×10^{-2}	$6.10\text{E}-25$	11.23	3540
	$>\text{C}(\text{OO}^\bullet)-$	4.60×10^{-5}	$6.74\text{E}-03$	3.9	8104
$=\text{C}-\text{CH}<$	$-\text{CH}_2\text{OO}^\bullet$ ^a	6.15×10^{-1}	$6.10\text{E}-25$	11.23	2595
	$>\text{CHOO}^\bullet$ ^a	1.87×10^0	$6.10\text{E}-25$	11.23	2263
	$>\text{C}(\text{OO}^\bullet)-$ ^{a,b}	1.30×10^{-2}	$6.10\text{E}-25$	11.23	3744
1,6-H-migration					
$=\text{C}-\text{CH}_2-$	$-\text{CH}_2\text{OO}^\bullet$	2.04×10^0	$8.49\text{E}-55$	20.84	-1928
	$>\text{CHOO}^\bullet$ ^{a,b}	7.68×10^{-2}	$7.71\text{E}-37$	15.05	1531
	$>\text{C}(\text{OO}^\bullet)-$	4.27×10^0	$7.72\text{E}-46$	17.86	-1061
$=\text{C}-\text{CH}<$	$-\text{CH}_2\text{OO}^\bullet$ ^a	7.39×10^{-1}	$7.71\text{E}-37$	15.05	857
	$>\text{CHOO}^\bullet$ ^{a,b}	6.69×10^0	$7.71\text{E}-37$	15.05	200
	$>\text{C}(\text{OO}^\bullet)-$	4.17×10^{-3}	$6.99\text{E}-10$	6.43	6275
1,7-H-migration					
$=\text{C}-\text{CH}_2-$	$-\text{CH}_2\text{OO}^\bullet$	8.22×10^0	$4.62\text{E}-48$	18.62	-1503
	$>\text{CHOO}^\bullet$ ^{a,b}	2.55×10^{-2}	$4.62\text{E}-48$	18.62	219
	$>\text{C}(\text{OO}^\bullet)-$ ^{a,b}	5.70×10^{-3}	$4.62\text{E}-48$	18.62	665
$=\text{C}-\text{CH}<$	$-\text{CH}_2\text{OO}^\bullet$ ^a	3.56×10^{-1}	$4.62\text{E}-48$	18.62	-568
	$>\text{CHOO}^\bullet$ ^{a,b}	2.27×10^0	$4.62\text{E}-48$	18.62	-1120
	$>\text{C}(\text{OO}^\bullet)-$ ^{a,b}	4.30×10^{-1}	$4.62\text{E}-48$	18.62	-624

^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