

H-migration in alkyl peroxy radicals under atmospheric conditions

— Supporting information —

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1. Additional information on methodologies

1.1 Software

The quantum chemical calculations were performed using the following software suites:

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery Jr., J. A., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Keith, T., Kobayashi, R., Normand, J., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J., Fox, D. J. and Pople, J. A.: Gaussian 09, Revision B.01, Gaussian Inc., Wallington CT., 2010.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A. V., Bloino, J., Janesko, B. G., Gomperts, R., Mennucci, B., Hratchian, H. P., Ortiz, J. V., Izmaylov, A. F., Sonnenberg, J. L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V. G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Eara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Mntgomery, Jr., J. A., Peralta, J. E., Ogliaro, F., Bearpark, M. J., Heyd, J. J., Brothers, E. N., Kudin, K. N., Staroverov, V. N., Keith, T. A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A. P., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Millam, J. M., Klene, M., Adamo, C., Cammi, R., Ochterski, J. W., Martin, R. L., Morokuma, K., Farkas, O., Foresman, J. B. and Fox, D. J.: Gaussian 16, Revision B.01, Gaussian Inc., Wallington CT., 2016.

1.2. Quantum chemical methodologies for geometry optimization

The following quantum chemical methodologies were used to optimize geometries and calculate vibrational frequencies:

M05-2X/6-311G(d,p)
M05-2X/6-311+G(2df,2p)
M05-2X/aux-cc-pVDZ
M05-2X/aux-cc-pVTZ
M06-2X/6-311+G(2df,2p)
M06-2X/cc-pVDZ
M06-2X/cc-pVTZ
M06-2X/aug-cc-pVTZ
M06-2X-D3/aug-cc-pVTZ
M06-2X/aug-cc-pVQZ
B3LYP/6-31G(d,p) 5 d-orbitals
B3LYP/6-31+G(d,p) 6 d-orbitals
B3LYP/6-31G(2df,p) 6 d-orbitals (used in G3X/G3SX calculations)
B3LYP/6-311G(d,p)
B3LYP/6-311G(2d,d,p) (used in CBS-QB3)
B3LYP/6-311+G(2d,p) 5 d-orbitals
B3LYP/aux-cc-pVDZ
B3LYP/aux-cc-pVTZ
QCISD/6-311G(d,p) (used in CBS-APNO)

Of this list we preferentially use a limited set, to reduce methodological differences somewhat. The most commonly used level of theory is B3LYP/6-31G(d,p) with 5 d-orbitals, M05-2X/6-311G(d,p), and M06-2X/aux-cc-pVTZ. The most accurate of these is the latter methodology, which is used in our recent rate coefficient calculations; the conformers are typically optimized first at the M06-2X/cc-pVDZ level of theory, and re-optimized using the larger basis set.

1.3. Quantum chemical methodologies used in single-point energy calculations

In addition to the energy information obtained at the same level as the geometry optimization, single point energy calculations are performed at the following levels of theory to obtain more accurate energies:

G3X
G3SX
CBS-QB3
CBS-APNO
CCSD(T)/6-31+G(d') (used in CBS-QB3 calculations)
CCSD(T)/6-311G(d,p)
CCSD(T)/6-311G(2d,p)
CCSD(T)/aug-cc-pVDZ
CCSD(T)/aug-cc-pVTZ

CCSD(T)/aug-cc-pVQZ
 QCISD(T)/6-311++G(2df,p) (used in CBS-APNO calculations)
 QCISD(T)/6-31G(d) (used in G3X, G3SX calculations)

1.4 Complete basis set (CBS) energy calculations

We performed CCSD(T) calculations extrapolated to the complete basis set (CBS); these calculations use aug-cc-pVxZ (x = D, T, Q) basis sets, using the aug-Schwartz4(DT) and aug-Schwartz6(DTQ) extrapolation scheme as described by Martin et al. (1996). Table 1 below lists a set of CCSD(T)/CBS barrier heights compared to the barrier height used in the SAR development. The methodology indicated are the level of theory used for the geometry, and the basis sets used in the CBS extrapolation (2 or 3 basis sets using the 'x' values described above). The CBS data are not used in the derivation of the SAR, but they give an idea of how sensitive the barrier heights are to the level of theory. All in all, CBS extrapolations reduce the uncertainty by a few tenths of a kcal mol⁻¹ on the barrier height, and are thus able to reduce methodological scatter on the k(298 K) rate coefficients by a factor 1.5 to 2. As such, they appear to be less rewarding for the computational cost, considering the uncertainties on e.g. the tunneling corrections and the IRCMax calculations (see below).

Methodology:

A : M05-2X/6-311G(d,p)
 B : B3LYP/6-31G(d,p)
 C : M05-2X/aug-cc-pVDZ
 D : M05-2X/aug-cc-pVTZ
 E : B3LYP/6-31+G(d,p)
 F : B3LYP/aug-cc-pVDZ

Table 1: Comparison between the barrier heights (kcal mol⁻¹) used in the kinetic calculations, and improved CCSD(T)/CBS calculations.

Reactant	Product	E _b (used)	E _b (CBS)	Meth.
•OOCH ₂ -CH ₂ -CH ₃	HOCH ₂ -CH ₂ -C•H ₂	25.3	25.29 (DTQ)	A
			24.57 (DT)	B
Z-•OOCH ₂ -CH=C(CH ₃)-CH ₂ OH	Z-HOCH ₂ -CH=C(CH ₃)-C•HOH	19.38	19.28 (DT)	A
			19.30 (DT)	C
			19.45 (DT)	D
			19.47 (DT)	E
			19.49 (DT)	F
•OOCH(CH ₃)-CH ₂ -CH ₂ -CHOH-CH ₃	HOCH(CH ₃)-CH ₂ -CH ₂ -C•OH-CH ₃	16.88	16.88 (DT)	A
HOCH ₂ -CH(OO•)-CH=O	HOCH ₂ -CH(OOH)-C•=O	20.99	20.82 (DT)	A
HOCH ₂ -C(CH ₃)(OO•)-CH=O	HOCH ₂ -C(CH ₃)(OOH)-C•=O	20.54	20.38 (DT)	A
•OOCH ₂ -C(O)OH	HOCH ₂ -C(O)O• → OH+CH ₂ O+CO ₂	19.98	20.00 (DTQ)	A
HOCH ₂ -C(CH ₃)(OO•)-C=O(OH)	HOCH ₂ -C(CH ₃)(OOH)-C(O)O• → ...	19.36	18.72 (DT)	A
•OOCH ₂ -CH ₂ -CH ₂ -CH ₃	HOCH ₂ -CH ₂ -C•H-CH ₃	22.78	22.61 (DT)	A

Reference

Martin, J. M. L.: Ab initio total atomization energies of small molecules — towards the basis set limit, Chem. Phys. Lett., 259(5–6), 669–678, doi:[10.1016/0009-2614\(96\)00898-6](https://doi.org/10.1016/0009-2614(96)00898-6), 1996.

1.5 IRCMax calculations

Some of the quantum chemical methodologies are prone to yielding transition state geometries that are positioned not at the true transition state saddle point, but some (small) distance away, likely towards the products or reactants. This leads to erroneous reaction activation energies. Performing higher-level single point energy calculations on these geometries does not alleviate the problem. IRCMax calculations (Malick et al. 1998) can partially address this problem by performing a series of calculations along the IRC (intrinsic reaction coordinate) trajectory near the TS geometry, and locating the highest energy point along this lower-energy path; this energy maximum is a better estimate of the TS barrier height that would have been obtained by re-optimizing the geometry at the higher level of theory. The method is not able to correct for geometry distortions that are not along the IRC path.

We have performed a series of IRCMax calculations to probe the sensitivity of our predictions to this problem. In Table 2 below we list the energy difference between a higher-level single point energy calculations at the transition state geometry obtained using a lower level of theory, and the highest energy obtained at that higher-level methodology when calculation additional points along the IRC path. We find that B3LYP-based transition state geometries differ strongly from those at higher levels of theory, leading to errors on the energy calculations of up to a kcal mol⁻¹; these geometries thus add an additional uncertainty of up to a factor 5 on the predicted k(298 K) rate coefficients. M05-2X and M06-2X geometries are much more reliable, and are generally at or very near the optimal IRCMax geometry, inducing errors of 20% or less on the k(298 K) values. As the training and test data sets for the SAR extensively use B3LYP geometries, the resulting increased scatter introduces additional uncertainty on the SAR predictions. The only solution is to redo all calculations at a higher level of theory, avoiding B3LYP-based data in the SAR.

Table 2: IRCMax calculations for a set of methodologies, listing the difference between the TS geometry energy and the IRCMax energy (kcal mol⁻¹)

Reactant	Product	Methodology	ΔE
*OOCH ₂ -CH ₂ -CH ₃	HOOCH ₂ -CH ₂ -C*H ₂	CBS-QB3//B3LYP/CBSB7	0.22
		CBS-QB3//M05-2X/6-311G(d,p)	0.00
		CBS-APNO//M05-2X/6-311G(d,p)	0.00
		CCSD(T)/aug-cc-pVDZ//M05-2X/6-311G(d,p)	0.00
*OOCH ₂ -CH ₂ -CH ₂ -CH ₃	HOOCH ₂ -CH ₂ -C*H-CH ₃	CBS-QB3//B3LYP/CBSB7	0.24
OOCH ₂ -CH ₂ -CH(CH ₃)-CH ₃	HOOCH ₂ -CH ₂ -C(CH ₃)-CH ₃	CBS-QB3//B3LYP/CBSB7	0.26
		CBS-QB3//M05-2X/6-311G(d,p)	0.00
*OOCH ₂ -CH=CH-CH ₃	HOOCH ₂ -CH=CH-C*H ₂	CBS-QB3//B3LYP/CBSB7	0.11
		CBS-QB3//B3LYP/6-31+G(d,p)	0.08
		CBS-QB3//M05-2X/6-311G(d,p)	0.00
Z-*OOCH ₂ -CH=C(CH ₃)-CH ₂ OH	Z-HOOCH ₂ -CH=C(CH ₃)-C*HOH	CBS-QB3//B3LYP/6-31+G(d,p)	0.69
		CBS-APNO//B3LYP/6-31+G(d,p)	0.19
		G3SX//B3LYP/6-31G(2df,p)	0.11
		CBS-QB3//M05-2X/6-311G(d,p)	0.03
		CBS-APNO//M05-2X/6-311G(d,p)	0.00
Z-*OOCH ₂ -C(CH ₃)=CH-CH ₂ OH	Z-HOOCH ₂ -C(CH ₃)=CH-C*HOH	CBS-QB3//B3LYP/6-31+G(d,p)	0.47
		G3SX//B3LYP/6-31G(2df,p)	0.10
		CBS-QB3//M05-2X/6-311G(d,p)	0.00
		CBS-APNO//M05-2X/6-311G(d,p)	0.01
*OOCH(CH ₃)-CH ₂ -CH ₂ -CH ₂ OH	HOOC(CH ₃)-CH ₂ -CH ₂ -C*HOH	CBS-QB3//B3LYP/CBSB7	0.39
		CBS-QB3//B3LYP/6-31+G(d,p)	0.45
		CBS-QB3//M05-2X/6-311G(d,p)	0.00
		CBS-APNO//M05-2X/6-311G(d,p)	0.04

HOCH ₂ -CH(OO*)-CH=O	HOCH ₂ -CH(OOH)-C*=O	CBS-QB3//B3LYP/CBSB7	1.04
		CBS-QB3//B3LYP/6-31G(2df,p)	1.01
		G3SX//B3LYP/6-31G(2df,p)	0.43
		CBS-QB3//M05-2X/6-311G(d,p)	0.13
		CCSD(T)/aug-cc-pVDZ//M05-2X/6-311G(d,p)	0.12
		CCSD(T)/aug-cc-pVTZ//M05-2X/6-311G(d,p)	0.06
HOCH ₂ -C(CH ₃)(OO*)-CH=O	HOCH ₂ -C(CH ₃)(OOH)-C*=O	CBS-QB3//B3LYP/CBSB7	1.12
		CBS-QB3//M05-2X/6-311G(d,p)	0.17
		CCSD(T)/aug-cc-pVDZ//M05-2X/6-311G(d,p)	0.12
		CBS-APNO//M05-2X/6-311G(d,p)	0.06
OOCH ₂ -C(O)OH	HOOCH ₂ -C(O)O → CO ₂ + OH + HCHO	G3SX//B3LYP/6-31G(2df,p)	2.40
		CBS-QB3//M05-2X/6-311G(d,p)	0.00
		CCSD(T)/aug-cc-pVDZ//M05-2X/6-311G(d,p)	0.00
		CCSD(T)/aug-cc-pVTZ//M05-2X/6-311G(d,p)	0.00
		CBS-APNO//M05-2X/6-311G(d,p)	0.08

Reference

Malick, D. K., Petersson, G. A. and Montgomery, J. A.: Transition states for chemical reactions I. Geometry and classical barrier height, J. Chem. Phys., 108(14), 5704–5713, doi:[10.1063/1.476317](https://doi.org/10.1063/1.476317), 1998.

1.6 Relative multi-conformer transition state theory (rel-MC-TST)

Relative multi-conformer transition state theory (rel-MC-TST) leverages MC-TST (Vereecken and Peeters, 2003) rate coefficients calculation on a reference reaction to obtain estimates of rate coefficients of "similar" reactions relative to the reference reaction at a reduced cost. The required quantum chemical calculations are all conformers for the MC-TST rate coefficient of the reference calculation, and a small set of additional calculations on selected conformers of the target reaction. A formal derivation, and benchmarking, will be published in an upcoming publication; we limit ourselves here to a brief outline of the approach, and provide a minimum number of equations.

1.6.1. Brief outline of rel-MC-TST

The rate of any target reaction can be written as a temperature-dependent ratio $R(T)$ between the rate coefficient of a reference reaction and that of the target reaction;

$$k_{target}(T) = k_{ref}(T) \times R(T) \quad (\text{E.S1})$$

MC-TST expresses a rate coefficient in a transition state paradigm, explicitly summing the contributions of the reactant(s) and transition state (TS) conformers by their respective partition functions:

$$k(T) = \frac{kT}{h} \times \frac{\sum_i \kappa_i(T) Q_i^{\ddagger}(T) \exp\left(\frac{-E_i}{kT}\right)}{\sum_i Q_A^i(T) \exp\left(\frac{-E_i}{kT}\right)} \times \exp\left(\frac{-E_b}{kT}\right) \quad (\text{E.S2})$$

where $Q_i(T)$ indicates the partition function (usually in a rigid rotor harmonic oscillator approximation) for conformer i at temperature T (A signifies the reactant, \ddagger is the TS with exclusion of the reaction coordinate mode), E_i the conformer ZPE-corrected energy relative to the lowest conformer, E_b the energy difference between the energetically lowest conformers of reactant and transition state; k is the Boltzmann constant and h Planks constant. κ_i is the tunneling correction; typically, this correction is taken identical for all conformers, e.g. an Eckart tunneling correction for the lowest conformer.

The ratio $R(T)$ can be expressed as a ratio of partition functions and Boltzmann-weighted reaction energies for the reference and target reaction, which in turn can be compacted to a ratio of rate coefficients:

$$k_{target}(T) = k_{ref}(T) \times \left(\frac{\sum_i \kappa_{target}^i(T) Q_{target}^{\ddagger,i}(T) \exp\left(\frac{-E_{target}^i}{kT}\right)}{\sum_i \kappa_{ref}^i(T) Q_{ref}^{\ddagger,i}(T) \exp\left(\frac{-E_{ref}^i}{kT}\right)} \right) \times \left(\frac{\sum_i Q_{ref}^{A,i}(T) \exp\left(\frac{-E_{ref}^i}{kT}\right)}{\sum_i Q_{target}^{A,i}(T) \exp\left(\frac{-E_{target}^i}{kT}\right)} \right) \times \exp\left(\frac{-(E_{target}^b - E_{ref}^b)}{kT}\right) \quad (E.S3)$$

$$= k_{ref}(T) \times \frac{k_{target}(T)}{k_{ref}(T)}$$

which is trivially true if the ratio is calculated using all conformers (full MC-TST) for both reactions. Relative MC-TST consists of approximating the ratio by using only a selected set of conformers for reactant and transition states:

$$k_{target}(T) = k_{ref}(T) \times \frac{k_{target}^{selected}(T)}{k_{ref}^{selected}(T)} \quad (E.S4)$$

where the approximation becomes better as more conformers are included in the selection, up to the limit of including all conformers. In the ratio, one uses a similar (limited) number and type of conformers for both the reference and target reaction. Essentially, this approach samples the ratio of entropy and energy of corresponding reactant and transition state conformers between reference and target reaction, and the difference in reaction barrier height that implies. In as much as the average change in molecular structure is represented in the properties of the selected conformers, this provides an estimate of the target rate coefficient without having to calculate all conformers of the target reaction. Furthermore, given that some conformers have a larger contribution to the populations, or are more representative for the molecular change between reference and target reaction, a judicious choice of conformers led by chemical knowledge can lead to rapid convergence of the ratio. A good selection will thus choose conformers that contribute strongly, choose conformers in reference and target reaction that correspond as well as possible, choose conformers that represent the change in molecular structure between reference and target best (e.g. absence/presence of H-bonding), and choose the included number of conformers in reference and target to correct for changes in number of total conformers (e.g. changes in number of internal rotors due to a new double bond in the target molecule). In the extreme limit, even a single, well-chosen conformer each for reactant and TS can be sufficient to obtain a fair estimate of the ratio.

1.6.2 Benefits of rel-MC-TST

A key benefit of rel-MC-TST is that the selection of the conformers is guided by the information from the MC-TST analysis of the reference reaction, based on information on all conformers. Intrinsically, the target rate coefficient is then indirectly based on information on all conformers, through the ratios of properties; this ratio is often similar across many/most conformers. The selection of the most representative conformers, and generating starting geometries for the modified molecular structure of the target conformers, benefits greatly from the full-conformer information available from the analysis of the reference reaction. Aided with some chemical knowledge, one can then readily characterize a small selection of conformers of the target reaction and calculate the rate ratio with fair confidence. Rel-MC-TST is particularly useful for theoretical work aimed at structure-activity relationships, as there one performs a systematic set of changes on a base molecular structure. It is also useful for the theoretical characterization of reaction mechanism; examples include the study of isoprene or terpenoid oxidation mechanisms, which often involve similar molecules undergoing similar reactions, changing only in the positioning of the (spectator) substituents.

Møller et al. (2016) have described an approximation to MC-TST to reduce the computational cost, implemented by generating a limited number of conformers at a very low level of theory rather than attempting a near-exhaustive characterization of the full population. However, as discussed briefly by Novelli et al. (2019), the proposed conformer selection process based on semi-empirical methods does not reliably generate the most contributing conformers, leading to a large *a priori* uncertainty of 1 to 2 orders of magnitude, though the method often yields good results if the reaction studied is amenable to cancellation of error. An earlier implementation (Zhang and Dibble, 2011) of this technique using semi-empirical methods to generate conformers was likewise found to miss important conformers. Compared to the approximation by Møller et al. (2016), the rel-MC-TST technique described here is more robust even with a small selection of conformers, as full-conformer information from the reference reaction is easily used to ensure the best possible estimate for the least amount of effort, without risking unknown omissions. It is also more cost-effective, as one does not need to generate conformers from scratch for each reaction. Indeed, a single (costly) MC-TST reference

rate coefficient can be used to cheaply generate estimates for many target reaction rate coefficients. The current study, for example, uses the four 1-hexylperoxy H-migrations (spans 1,5 through 1,8) as a reference for 27 reactions. Given that especially for reactions involving a cyclic TS the main computational effort lies in characterizing the multitude of reactant conformers, as the TS conformers are relatively few. Finally, the selected set of conformers can be systematically enlarged, characterizing additional conformers for the target reaction until convergence is obtained, thus allowing easy balancing of computational cost versus accuracy.

1.6.3 Application of rel-MC-TST in the current work

Section 3 lists a set of rate coefficients derived using rel-MC-TST, and the rate coefficient they are based on. Although we do not describe benchmarks of rel-MC-TST at this time, we find that the rate coefficients for which we have target $k(T)$ values, the rate coefficients predicted by rel-MC-TST usually fit well within the SAR framework. In a few cases, deviations of over 1 order of magnitude are suspected. However, we have applied rel-MC-TST in an extreme way, using 1 to 6 conformers only, truly a bare minimum. The overall good performance is a good indicator of the robustness of the method. A future paper benchmarking the approximation will make recommendations regarding the number of conformers to use, and how to select the most representative conformers.

2. Absolute rate coefficient predictions

All rate coefficients in this section are calculated using MC-TST, incorporating all conformers.

Methodologies:

- A CCSD(T)/aug-cc-pVTZ//M06-2X-D3/aug-cc-pVTZ
- B CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ
- C CBS-APNO//B3LYP/6-31G(d,p)
- D CCSD(T)/aug-cc-pVTZ//M05-2X/6-311G(d,p)
- E CBS-QB3//B3LYP/6-31G(d,p)
- F CBS-APNO//M05-2X/6-311G(d,p)
- G CBS-QB3//M05-2X/6-311G(d,p)
- H CCSD(T)/CBS//M06-2X-aug-cc-pVTZ
- I G3SX

Reactant	Span	Subst. OO / H	Method	k(298K) / s ⁻¹	A / s ⁻¹	n	E _a / K
*OO-CH ₂ -CH ₂ -CH ₃	1,5	1° / 1°	A	6.04×10 ⁻⁶	6.20E-34	14.32	5108
OO-CH ₂ -CH ₂ -CH ₂ -CH ₃	1,6	1° / 1°	B	2.76×10 ⁻⁴	4.84E-22	10.46	5565
OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	1,5	1° / 2°	B	4.39×10 ⁻⁴	2.27E-20	9.91	5654
	1,6	1° / 2°	B*	6.58×10 ⁻⁴	1.15E-14	7.85	5941
	1,7	1° / 1°	B*	3.82×10 ⁻⁶	2.02E-16	8.16	6806
CH ₃ -CH ₂ (OO*)-CH ₂ -CH ₂ -CH ₃	1,5	2° / 2°	B*	1.01×10 ⁻³	8.68E-19	9.46	5718
	1,6	2° / 1°	B*	8.81×10 ⁻⁶	7.28E-16	8.31	7183
*OO-CH ₂ -CH ₂ -CH(CH ₃)-CH ₃	1,5	1° / 3°	C	2.87×10 ⁻²	1.39E-02	4	6572
OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	1,5	1° / 2°	B	5.93×10 ⁻⁴	1.97E-19	9.61	5690
	1,6	1° / 2°	B*	9.50×10 ⁻⁴	1.38E-13	7.51	5990
	1,7	1° / 2°	B*	3.43×10 ⁻⁴	1.10E-18	8.91	5172
	1,8	1° / 1°	B*	4.92×10 ⁻⁸	4.73E-25	10.7	6489

$\bullet\text{OO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH(CH}_3\text{)-CH}_3$	1,6	1° / 3°	D	2.19×10^{-2}	1.67E-03	4.27	6482
$\bullet\text{OO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH(CH}_3\text{)-CH}_3$	1,7	1° / 3°	E	2.43×10^{-1}	5.58E-11	6.53	4472
$\bullet\text{OO-CH}_2\text{-CH(CH}_3\text{)-CH}_2\text{-CH}_2\text{-CH(CH}_3\text{)-CH}_3$	1,5	1° / 1°	B	7.86×10^{-6}	1.64E-31	13.55	5381
	1,5	1° / 2°	B	4.00×10^{-3}	6.89E-40	16.23	2326
	1,6	1° / 2°	B	5.99×10^{-3}	1.59E-27	12.04	3576
	1,7	1° / 3°	B	5.76×10^{-2}	1.07E-41	16.28	375
	1,8	1° / 1°	B	1.48×10^{-7}	3.20E-29	12.1	5678
$\text{CH}_3\text{-C(CH}_3\text{)(OO}\bullet\text{)-CH}_2\text{-CH}_2\text{-CH(CH}_3\text{)-CH}_3$	1,5	3° / 2°	B	1.38×10^{-3}	1.00E-29	13.06	4235
	1,6	3° / 3°	B	8.94×10^{-2}	1.28E-35	14.71	1747
	1,7	3° / 1°	B	2.47×10^{-5}	4.57E-25	10.98	5094
$\text{CH}_3\text{-CH(CH}_3\text{)-CH(OO}\bullet\text{)-CH}_2\text{-CH(CH}_3\text{)-CH}_3$	1,5	2° / 1°	B	3.96×10^{-5}	1.31E-27	12.46	5719
	1,5	2° / 3°	B	9.02×10^{-2}	1.64E-35	14.99	2286
	1,6	2° / 1°	B	5.55×10^{-5}	6.75E-29	12.73	5196
$\text{Z-}\bullet\text{OO-CH=CH-CH}_2\text{-CH}_3$	1,5	2° / 2° endo=	E	9.24×10^{-2}	2.30E-76	28.7	-2469
$\text{Z-}\bullet\text{OO-CH}_2\text{-CH=CH-CH}_3$	1,6	1° / 2° endo=	E	2.17×10^{-2}	3.94E-75	27.57	-3115
$\text{Z-}\bullet\text{OO-C(CH}_3\text{)=CH-CH}_3$	1,5	2° / 1° endo=	E	2.95×10^{-3}	1.02E-89	33.22	-2935
$\text{Z-}\bullet\text{OO-CH=C(CH}_3\text{)-CH}_3$	1,5	2° / 1° endo=	E	4.24×10^{-4}	1.91E-95	35.01	-3246
$\text{Z-}\bullet\text{OO-CH}_2\text{-CH=CH-CH}_2\text{-CH}_3$	1,6	1° / 2° endo=	E	6.38×10^{-1}	2.29E-69	25.74	-3268
$\text{Z-}\bullet\text{OO-CH}_2\text{-CH}_2\text{-CH=CH-CH}_3$	1,7	1° / 2° endo=	E	1.18×10^0	8.54E-60	22.36	-2615
$\bullet\text{OO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH=CH}_2$	1,5	1° / 2° exo=	E	1.69×10^0	4.43E-63	23.77	-2595
$\text{Z-}\bullet\text{OO-CH=CH-CH(CH}_3\text{)-CH}_3$	1,5	2° / 3° endo=	E	8.57×10^{-1}	7.44E-68	25.98	-1906
$\text{Z-}\bullet\text{OO-CH}_2\text{-C(CH}_3\text{)=CH-CH}_3$	1,6	1° / 1° endo=	E	4.05×10^{-2}	5.49E-75	27.56	-3219
$\text{Z-}\bullet\text{OO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH=CH-CH}_3$	1,5	1° / 2° exo=	E	1.88×10^0	8.20E-62	23.31	-2529
$\text{E-}\bullet\text{OO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH=CH-CH}_3$	1,5	1° / 2° exo=	E	2.30×10^0	1.54E-61	23.31	-2410
$\bullet\text{OO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH=CH}_2$	1,6	1° / 2° exo=	E	3.12×10^0	1.88E-56	21.38	-2277
$\text{Z-}\bullet\text{OO-CH}_2\text{-CH=CH-CH(CH}_3\text{)-CH}_3$	1,6	1° / 3° endo=	E	1.35×10^1	1.20E-56	21.76	-2204

Z-•OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=CH-CH ₃	1,6	1° / 2° exo=	E	6.21×10 ⁰	6.97E-53	20.19	-2064
E-•OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=CH-CH ₃	1,6	1° / 2° exo=	E	3.90×10 ⁰	4.68E-55	20.96	-2104
•OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=CH ₂	1,7	1° / 2° exo=	E	7.16×10 ⁰	7.85E-56	21.15	-2497
•OO-CH(CH ₃)-CH-CH ₂ -CH ₂ -CH ₂ OH	1,6	2° / 2°(OH)	E	1.19×10 ⁰	3.54E+08	0.5	6665
•OO-CH(CH ₃)-CH-CH ₂ -CH ₂ -CH(OH)-CH ₃	1,6	2° / 3°(OH)	E	5.50×10 ⁻¹	2.51E-01	3.42	5577
•OO-CH ₂ -CH ₂ -CH=O	1,5	1° / 3°(=O)	E	4.84×10 ⁰	1.96E-39	16.21	492
			C	9.74×10 ⁰	3.66E-37	15.46	573
•OO-CH ₂ -CH ₂ -CH ₂ -CH=O	1,6	1° / 3°(=O)	E	4.94×10 ⁰	2.03E-41	16.79	101
•OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=O	1,7	1° / 3°(=O)	E	1.83×10 ⁰	2.91E-30	12.9	1458
(R,R) O=CH-C(CH ₃)(OO•)-CH(OOH)-CH ₂ (OOH)	1,4	3° / 3°(=O)	B*	1.15×10 ⁰	1.21E-83	30.69	-4811
	1,4	3° / 3°(OOH)	B*	4.88×10 ⁻³	4.59E-82	28.94	-3276
	1,5	3° / 2°(OOH)	B*	1.18×10 ⁻⁵	2.87E-35	15.11	3586
	1,6	3° / OOH	B*	1.84×10 ⁴	7.26E-40	15.39	-3656
	1,7	3° / OOH	B*	6.29×10 ⁴	2.75E-25	10.85	-1725
(R,R) O=CH-C(CH ₃)(OOH)-CH(OO•)-CH ₂ (OOH)	1,5	2° / 3°(=O)	B*	3.34×10 ¹	1.12E-67	25.15	-4273
	1,6	2° / OOH (primary)	B*	1.88×10 ⁴	1.17E-34	13.27	-3683
	1,6	2° / OOH (tertiary)	B*	2.97×10 ⁴	1.36E-38	14.73	-4035
(R,R) O=CH-C(CH ₃)(OOH)-CH(OOH)-CH ₂ (OO•)	1,6	1° / 3°(=O)	B*	2.28×10 ⁰	3.57E-41	16.93	788
	1,6	1° / OOH	B*	2.35×10 ³	3.06E-33	13.03	-2486
	1,7	1° / OOH	B*	1.27×10 ⁴	1.35E-22	9.96	-906
(R,S) O=CH-C(CH ₃)(OO•)-CH(OOH)-CH ₂ (OOH)	1,4	3° / 3°(=O)	B*	3.71×10 ⁰	7.07E-75	27.88	-3914
	1,4	3° / 3°(OOH)	B*	8.44×10 ⁻⁵	2.52E-68	24.59	-1817
	1,5	3° / 2°(OOH)	B*	5.02×10 ⁻²	8.69E-27	12.33	3989
	1,6	3° / OOH	B*	6.34×10 ⁴	7.94E-17	7.46	-1680
	1,7	3° / OOH	B*	6.20×10 ⁴	4.02E-20	9.43	-579
(R,S) O=CH-C(CH ₃)(OOH)-CH(OO•)-CH ₂ (OOH)	1,5	2° / 3°(=O)	B*	3.05×10 ⁻¹	4.28E-75	28.3	-2589

	1,6	2° / OOH (primary)	B*	1.32×10 ³	4.40E-22	9.34	-926
	1,6	2° / OOH (tertiary)	B*	2.07×10 ³	7.58E-19	7.91	-1277
(R,S) O=CH-C(CH ₃)(OOH)-CH(OOH)-CH ₂ (OO*)	1,6	1° / 3°(=O)	B*	4.86×10 ¹	6.99E-37	15.2	-133
	1,6	1° / OOH	B*	9.89×10 ³	7.65E-28	11.39	-1308
	1,7	1° / OOH	B*	1.52×10 ³	6.68E-28	11.93	-558
*OO-CH ₂ -C(=O)OH	1,5	1° / COOH	D	3.10×10 ⁻¹	2.42E-68	26.07	-1799
			I	3.42×10 ⁻²	3.45E+08	1.05	8647
*OO-CH(CH ₃)-C(=O)OH	1,5	2° / COOH	I	1.38×10 ⁰	1.44E+08	1.16	7472
CH ₂ (OH)-C(CH ₃)(OO*)-C(=O)OH	1,5	3° / COOH	D	1.60×10 ⁰	3.73E-54	21.18	-842
Z-*OO-CH ₂ -CH=C(CH ₃)-CH ₂ (ONO ₂)	1,6	1° / 2°(ONO ₂) endo=	B	1.90×10 ⁻²	7.72E-78	28.02	-4158
E-*OO-CH ₂ -CH=C(CH ₂ ONO ₂)-CH ₃	1,6	1° / 1° endo=	B	1.48×10 ⁻³	2.58E-84	30.21	-4128
*OO-C(CH ₃)(-CH=CH ₂)-CH ₂ (ONO ₂)	1,4	3° / 2°(ONO ₂)	B	1.84×10 ⁻⁸	8.78E-73	26.48	827
	1,4	3° / 1°	B	1.55×10 ⁻¹⁰	4.82E-75	27.35	2170
Z-*OO-CH ₂ -C(CH ₃)=CH-CH ₂ (ONO ₂)	1,6	1° / 2°(ONO ₂) endo=	B	5.35×10 ⁻²	2.52E-75	27.06	-4374
	1,5	1° / 1° gem=	B	3.28×10 ⁻⁴	1.07E-96	34.33	-5178
E-*OO-CH ₂ -C(CH ₃)=CH-CH ₂ (ONO ₂)	1,6	1° / 2°(ONO ₂) endo=	B	4.81×10 ⁻⁴	2.94E-97	34.68	-5088
CH ₂ (ONO ₂)-CH(OO*)-C(=CH ₂)-CH ₃	1,5	1° / 1° gem=	B	8.51×10 ⁻⁴	5.58E-89	32.05	-4050
*OO-CH ₂ -C(ONO ₂)(-CH=CH ₂)-CH ₃	1,5	1° / 1°	B	8.93×10 ⁻⁶	6.45E-40	16.3	4235
*OO-CH ₂ -CH(ONO ₂)-C(=CH ₂)-CH ₃	1,6	1° / 1° gem=	B	1.72×10 ⁻²	8.97E-67	24.55	-2426
CH ₃ -CH ₂ (OO*)-CH ₂ -CH ₂ -CH ₂ (OOH)	1,5	2° / 2°	B*	4.41×10 ⁻⁴	1.90E-35	14.77	3553
	1,6	2° / 2°(OOH)	B*	8.44×10 ⁻³	3.77E-40	15.89	1341
	1,8	2° / OOH	B*	1.17×10 ²	9.14E-15	6.76	423
OO-CH ₂ -CH ₂ -CH ₂ -CH(OOH)-CH ₃	1,5	1° / 2°	B	3.95×10 ⁻⁴	2.68E-38	15.73	3249
	1,6	1° / 3°(OOH)	B*	1.84×10 ⁻¹	1.07E-64	23.93	-2761
	1,7	1° / 1°	B*	3.18×10 ⁻⁷	1.18E-12	6.96	8093
	1,8	1° / OOH	B*	4.14×10 ²	3.48E-25	10.16	-1327

CH ₂ (OH)-CH(OO [•])-CH=O	1,4	2° / 3°(=O)	F	1.42×10 ⁰	1.88E-54	21.22	-947
			G	3.38×10 ⁻¹	2.31E-59	22.83	-1157
			D	3.97×10 ⁻²	1.08E-66	25.23	-1470
CH ₂ (OH)-C(CH ₃)(OO [•])-CH=O	1,4	3° / 3°(=O)	D	1.40×10 ⁻¹	2.54E-63	24.25	-1193
	1,5	3° / OH	D	1.32×10 ⁻⁶	9.32E+12	-0.61	11904
	1,4	3° / 2°(OH)	D	6.07×10 ⁻⁶	3.24E-44	17.66	3717
CH ₂ (OH)-CH(OO [•])-C(=O)-CH ₃	1,5	1° / 1°(endo-β=O)	D	4.94×10 ⁻⁵	2.94E+15	-1.35	11283
			H	3.84×10 ⁻⁵	2.05E-57	21.74	1083
	1,4	2° / 2°(OH)	H	3.19×10 ⁻⁵	3.11E-81	29.64	-1790
•OO-CH ₂ -CH(OH)-C(=O)-CH ₃	1,5	2° / OH	H	877×10 ⁻⁵	7.13E+11	-0.24	10571
	1,5	1° / OH	H	4.95×10 ⁻⁴	1.25E+11	-0.03	9897
	1,4	1° / 3°(OH)	H	1.46×10 ⁻²	5.87E-80	28.33	-4988
	1,6	1° / 1°(endo-β=O)	H	1.44×10 ⁻³	1.13E-35	14.61	2828
7-hydroxy-1-menthenyl-8-peroxy	1,5	cyclic	E	4.60×10 ⁻⁵	6.74E-03	3.9	8104
	1,6	cyclic	E	4.24×10 ⁻⁵	7.72E-46	17.86	-1061
2-hydroxy-1-menthenyl-8-peroxy	1,6	cyclic	E	4.16×10 ⁻³	6.99E-10	6.43	6275
pinonaldehydeperoxy	1,5	cyclic	E	8.70×10 ⁻⁵	3.17E-70	25.97	-815
	1,8	cyclic	E	3.66×10 ⁻⁶	7.65E-76	27.42	-1264
	1,9	cyclic	E	2.07×10 ⁻³	8.31E-49	18.83	808
1-hydroxymethyl-2-oxa-3,3-diMe-bicyclo[2.2.2]octane-syn-6-peroxy	1,5	cyclic	E	3.96×10 ⁻⁵	1.18E+06	1.92	7018
1-hydroxymethyl-2-oxa-3,3-diMe-bicyclo[2.2.2]octane-anti-6-peroxy	1,5	cyclic	E	8.60×10 ⁻²	7.75E-06	5.59	6710
•OOCH ₂ (OH)	1,3	1° / 2°(OH)	B	3.89×10 ⁻¹³	4.81E-199	69.16	-10187
	1,4	1° / OH	B	1.84×10 ³	1.17E+11	0.45	6127
•OOCH(OH) ₂	1,4	2° / OH	B	6.73×10 ⁷	7.93E+04	2.37	2018

* published in Novelli et al. (2019) ; Fuchs et al. (2018) ; Nozière and Vereecken (2019) ;

3. Relative rate coefficient predictions

All quantum chemical calculations are performed at the B3LYP/6-31G(d,p) (5 d-orbitals) level of theory. All rate coefficients in this section are calculated using rel-MC-TST, incorporating only a handful of conformers.

Reference molecules:

- A 1-hexylperoxy
- B 1-OH-4-pentylperoxy
- C 1-butene-1-peroxy
- D 2-pentene-1-peroxy
- E 3-pentene-1-peroxy
- F 4-pentene-1-peroxy
- G 5-hexene-1-peroxy
- H 6-heptene-1-peroxy

Reactant	Span	Subst. OO / H	Ref. Reaction	k(298K) / s ⁻¹	A / s ⁻¹	n	E _a / K
*OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	1,5	1° / 2°	A	4.55×10 ⁻⁴	2.22E+02	2.84	8719
	1,6	1° / 2°	A	1.33×10 ⁻³	4.53E+06	1.31	8770
	1,7	1° / 2°	A	1.65×10 ⁻³	1.43E+09	0.27	8643
	1,8	1° / 2°	A	1.31×10 ⁻⁵	7.76E-01	3.02	8396
*OO-CH ₂ -CH(OH)-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	1,5	1° / 2°(β-OH)	A	8.83×10 ⁻⁵	2.62E+02	2.91	9380
*OO-CH ₂ -C(=O)-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	1,5	1° / 2°(endo-β=O)	A	1.79×10 ⁻⁴	4.23E-74	27.41	-1251
	1,6	1° / 2°	A	9.86×10 ⁻⁵	7.79E-19	9.39	6267
*OO-CH ₂ -CH ₂ -CH(CH ₃)-CH ₂ -CH ₂ -CH ₂ -CH ₃	1,5	1° / 3°	A	4.55×10 ⁻²	2.75E-04	4.75	6539
*OO-CH ₂ -CH ₂ -CH(OH)-CH ₂ -CH ₂ -CH ₂ -CH ₃	1,5	1° / 3°(OH)	A	6.10×10 ⁻¹	5.54E-02	4.12	6277
	1,6	1° / 2°(β-OH)	A	3.07×10 ⁻⁴	4.34E+03	2.24	8702

*OO-CH ₂ -CH ₂ -C(=O)-CH ₂ -CH ₂ -CH ₂ -CH ₃	1,6	1° / 2°(endo-β=O)	A	7.61×10 ⁻³	1.47E-31	13.27	2825
	1,7	1° / 2°	A	1.03×10 ⁻⁵	4.88E-06	4.89	8075
*OO-CH ₂ -CH ₂ -CH ₂ -CH(CH ₃)-CH ₂ -CH ₂ -CH ₃	1,6	1° / 3°	A	2.16×10 ⁻²	7.40E-03	4.11	6651
*OO-CH ₂ -CH ₂ -CH ₂ -CH(OH)-CH ₂ -CH ₂ -CH ₃	1,5	1° / 2°(β-OH)	A	2.98×10 ⁻⁴	2.86E+12	-0.19	10640
	1,6	1° / 3°(OH)	B	7.58×10 ⁻¹	7.47E+12	-0.71	7708
	1,7	1° / 2°(β-OH)	A	3.09×10 ⁻⁵	4.65E+08	0.45	9804
*OO-CH ₂ -CH ₂ -CH ₂ -C(=O)-CH ₂ -CH ₂ -CH ₃	1,5	1° / 2°(exo-β=O)	A	8.81×10 ⁻²	7.64E-24	10.92	3402
	1,7	1° / 2°(endo-β=O)	A	3.08×10 ⁻³	6.17E-27	11.41	3108
*OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH(CH ₃)-CH ₂ -CH ₃	1,7	1° / 3°	A	1.56×10 ⁻³	1.53E-07	5.4	6415
*OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH(OH)-CH ₂ -CH ₃	1,6	1° / 2°(β-OH)	A	1.37×10 ⁻⁴	1.41E+02	2.69	8693
	1,7	1° / 3°(OH)	A	2.12×10 ⁻¹	1.17E-01	3.51	5782
*OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -C(=O)-CH ₂ -CH ₃	1,5	1° / 2°	A	7.20×10 ⁻⁵	1.32E-03	4.47	8457
	1,6	1° / 2°(exo-β=O)	A	1.99×10 ⁻²	4.48E-24	10.8	3484
*OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH(CH ₃)-CH ₃	1,8	1° / 3°	A	2.53×10 ⁻⁸	1.36E-22	10.11	7367
*OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH(OH)-CH ₃	1,7	1° / 2°(β-OH)	A	1.97×10 ⁻⁵	8.05E-08	5.8	8199
*OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -C(=O)-CH ₃	1,6	1° / 2°	A	3.07×10 ⁻⁵	9.50E-04	4.34	8383
	1,7	1° / 2°(endo-β=O)	A	9.43×10 ⁻³	9.01E-27	11.59	3187
Z-*OO-CH=CH-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	1,5	1° / 2° endo=	C	5.11×10 ⁻²	2.31E-94	34.58	-4675
Z-*OO-CH ₂ -CH=CH-CH ₂ -CH ₂ -CH ₂ -CH ₃	1,6	1° / 2° endo=	D	1.19×10 ⁻²	2.27E-70	26.02	-2292
	1,7	1° / 2°	A	8.53×10 ⁻⁵	2.17E-04	4.6	8081
Z-*OO-CH ₂ -CH ₂ -CH=CH-CH ₂ -CH ₂ -CH ₃	1,7	1° / 2° endo=	E	3.24×10 ⁰	1.83E-44	17.39	-836
Z-*OO-CH ₂ -CH ₂ -CH ₂ -CH=CH-CH ₂ -CH ₃	1,5	1° / 2° exo=	F	1.43×10 ⁰	8.16E-53	20.41	-1195
Z-*OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=CH-CH ₃	1,6	1° / 2° exo=	G	6.07×10 ⁰	5.42E-44	17.33	-802
Z-*OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=CH ₂	1,7	1° / 2° exo=	H	5.18×10 ⁰	3.18E-43	17.02	-761
Z-*OO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH=CH ₂ -CH ₃	1,7	1° / 2° exo=	H	1.45×10 ¹	3.94E-45	17.68	-1251

4. Spreadsheet for SAR derivation (FAIR)

In an attempt to make the SAR derivation more FAIR, we provide a spreadsheet that implements the derivation process as described in the main paper; for those that are unable to open the spreadsheet, a PDF version is also provided. For each of the SAR reaction classes, a set of 4 calculation blocks is provided, placed from left to right. The spreadsheet is an exact replication of the SAR derivation for the tables provided in the main text.

4.1 Literature data

The first block (see figure below) lists the reaction class (in the example below a 1,4-H-migration with a $-\text{CH}_2\text{OO}^\bullet$ peroxy radical and a migrating H-atom from a carbon bearing three hydrogen atoms ($-\text{CH}_3$). For the list of temperatures (column with header "T"), the available rate data is calculated, with indication of the source, and the parameters (P1, P2, P3) used in the kinetic expression, if any.

1,4 Hshift						
	P1	1.26E+12	5.6E+11	5.67E+13		1.00E-02
	P2	16930		0.2	1.88E+04	4.007
	P3		34.2	5.26E+08		12964
-CH2OO. -CH3	T	Miyoshi 2011	Sharma et al.	Otkjaer et al.	Otkjaer et al.	Zhang and Dibb
	200	2.17E-25	1.71E-26			1.17E-21
	225	2.64E-21	2.49E-22			2.53E-18
	250	4.90E-18	5.34E-19			1.23E-15
	260	6.62E-17	7.60E-18			1.05E-14
	270	7.39E-16	8.90E-17			7.77E-14
	280	6.94E-15	8.73E-16			4.99E-13
	290	5.58E-14	7.32E-15	9.24E-06		2.84E-12
	298	2.67E-13	3.62E-14	9.71E-06	3.72E-11	1.05E-11
	310	2.41E-12	3.42E-13	1.21E-05		6.63E-11
	320	1.33E-11	1.95E-12	1.62E-05		2.78E-10
	330	6.60E-11	1.00E-11			1.07E-09
	340	2.99E-10	4.67E-11			3.84E-09
	350	1.24E-09	1.99E-10			1.28E-08
	375	3.11E-08	5.37E-09			2.00E-07
	400	5.23E-07	9.57E-08			2.25E-06
	425	6.31E-06	1.22E-06			1.93E-05
	450	5.77E-05	1.17E-05			1.32E-04

A similar block is also used when calculating the average temperature dependence, when needed. Instead of kinetic data, the data columns will then contain rate predictions for SAR classes that are deemed useful for obtaining such an average temperature dependence. These blocks are marked with the "Average temperature dependence" title.

4.2 Selection of target k(298K) and temperature dependence

The second block lists the desired temperature dependence and target k(298K). If enough data of sufficient quality is available, this can be the geometric mean of the selected data. For those cases where not enough data is available to derive a temperature dependence, an average T-dependence will be linked from elsewhere on the sheet; such averaged T-dependencies are marked in **red**. In many cases, no suitable data is available to derive a k(298K) target value. The target value is then determined by using the averaged ratio between the substituted rates for those reactions where data is available, and the corresponding class for aliphatic peroxy radicals, i.e. the target reaction class will scale similar to the aliphatic RO_2 . Such averaged k(298K) targets are marked in **orange**. Finally, the T-dependence and the target k(298K) are merged, resulting in a "Final" rate coefficient curve that goes through the target k(298K) value and has a T-dependence scaled to that of the selected T-dependence.

A similar block is also used when calculating the average temperature dependence, when needed. The target k(298K) value and the "Final" column are in this case used merely to visualise the data (see below)

		Ea shift
		-1.12E+03
T-dependence	Target	Final
1.63E-24		4.34E-22
1.18E-20		1.69E-18
1.47E-17		1.28E-15
1.74E-16		1.28E-14
1.72E-15		1.08E-13
1.45E-14		7.79E-13
1.05E-13		4.93E-12
4.67E-13	1.98E-11	1.98E-11
3.79E-12		1.39E-10
1.93E-11		6.32E-10
8.92E-11		2.63E-09
3.77E-10		1.00E-08
1.47E-09		3.56E-08
3.22E-08		6.32E-07
4.83E-07		7.86E-06
5.29E-06		7.31E-05
4.46E-05		5.33E-04

4.3 Fitting to a (modified) Arrhenius expression

The temperature-dependent rate coefficient derived earlier is then fitted to both an Arrhenius expression $k(T) = A \times \exp(-E_a / T)$ and a modified Arrhenius expression $k(T) = A \times (T/K)^n \times \exp(-E_a / T)$. The parameters are listed in orange, and have units s^{-1} (A factors) and K (E_a factors); n is unit-less. The columns 1000/T, 1/T, log(1/T) and log(k) are used for the fitting procedure and for visualisation.

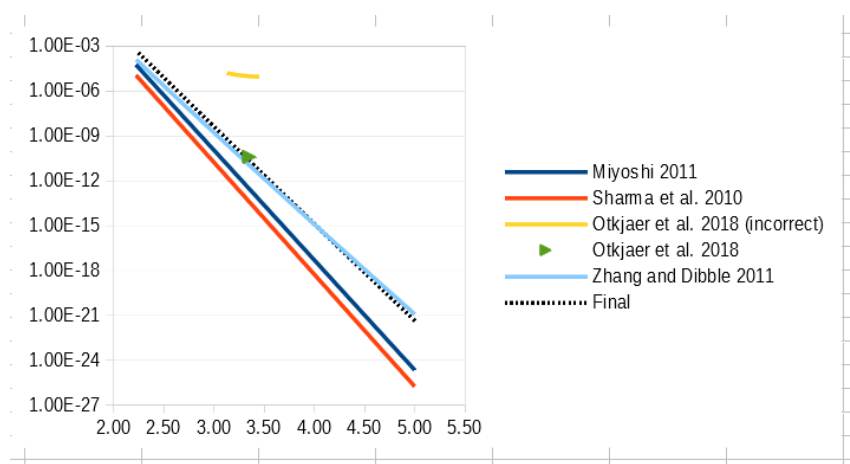
The goodness of recovery is probed by calculating the rate coefficient at the lowest and highest temperature, and calculating the ratio between the (modified) Arrhenius fit value and the original k(T) curve, to check if these extreme values are correctly replicated. This is given in the column "Replicate", which has an upper block with 4 values for the Arrhenius fit; the top value is k(lowest T), followed by the ratio for that T, and below that the k(highest T) value preceded by the ratio for that T. A similar block of 4 values is listed next to the modified Arrhenius parameters for that fit. The modified Arrhenius expression gives a near-perfect fit in all cases, and is used throughout; the quality of the fit for the traditional Arrhenius expression will depend strongly on the curvature in the Arrhenius plot.

1000/T	1/T	log(1/T)	log(-CH ₂ OO)	log(T)	Replicate
5.00	5.00E-03	-2.30E+00	-2.14E+01	A	3.97E-22
4.44	4.44E-03	-2.35E+00	-1.78E+01	1.48E+11	0.92
4.00	4.00E-03	-2.40E+00	-1.49E+01	Ea	
3.85	3.85E-03	-2.41E+00	-1.39E+01	1.50E+04	
3.70	3.70E-03	-2.43E+00	-1.30E+01		1.03
3.57	3.57E-03	-2.45E+00	-1.21E+01		8.03E-13
3.45	3.45E-03	-2.46E+00	-1.13E+01	-1.40E+00	
3.36	3.36E-03	-2.47E+00	-1.07E+01	-6.33E+03	
3.23	3.23E-03	-2.49E+00	-9.86E+00	7.08E+00	
3.13	3.13E-03	-2.51E+00	-9.20E+00	#N/A	
3.03	3.03E-03	-2.52E+00	-8.58E+00	#N/A	
2.94	2.94E-03	-2.53E+00	-8.00E+00	A	1.00E-08
2.86	2.86E-03	-2.54E+00	-7.45E+00	1.21E+07	1.00
2.67	2.67E-03	-2.57E+00	-6.20E+00	n	
2.50	2.50E-03	-2.60E+00	-5.10E+00	1.40	
2.35	2.35E-03	-2.63E+00	-4.14E+00	Ea	1.00
2.22	2.22E-03	-2.65E+00	-3.27E+00	14586	5.33E-04

4.4 Visualisation of the source data and final expression

For those SAR classes where there is literature data available, a plot is shown depicting $k(T) / s^{-1}$ against 1000 K / T. The available literature data is shown, either as a curve or as discrete values depending on the type of source data. The final SAR rate is also depicted as a dotted line.

Average temperature dependencies also have a plot, showing the source data, and the averaged T-dependence derived from that data; this serves only to visualize the averaging procedure.



4.5 Modifying or updating the SAR

The spreadsheet provided allows one to easily change the values used to derived the SAR expression, e.g. by adding data, removing data from the selection, or providing alternative $k(298K)$ target values or $k(T)$ temperature dependencies. Mostly, this involves only adding the data, and changing the underlying formulas to include / exclude the available data as wanted. No additional add-ins, macros, or scripts are necessary beyond the standard formulas of commonly used spreadsheet programs. The original spreadsheet was developed in Libreoffice, a freely downloadable Office suite.

5. Raw quantum chemical data

The most important quantum chemical data is provided in a separate text file, showing geometries, moments of inertia, vibrational wavenumbers, and (single point) energies, at all levels of theory where data is available.