

Supplementary Material for:

Estimation of rate coefficients and branching ratios for gas-phase reactions of OH with aliphatic organic compounds for use in automated mechanism construction

Contents

S1	Additional figures and tables	2
S2	SAR application examples for 298 K	15
	References	23

S1 Additional figures and tables

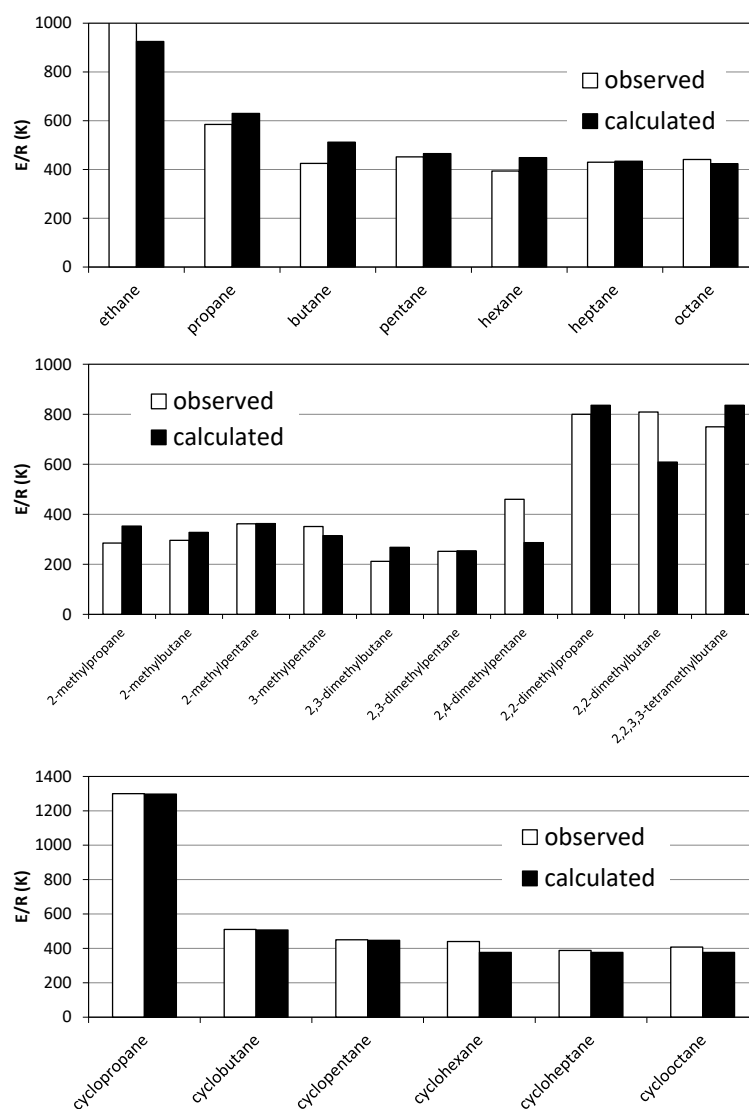


Figure S1. Comparison of observed (recommended) temperature coefficients (E/R) for the reactions of OH with 17 acyclic alkanes and 6 cyclic alkanes, compared with those estimated in the present work. The upper panel shows data for *n*-alkanes, the middle panel for branched alkanes, and the lower panel for cyclic alkanes.

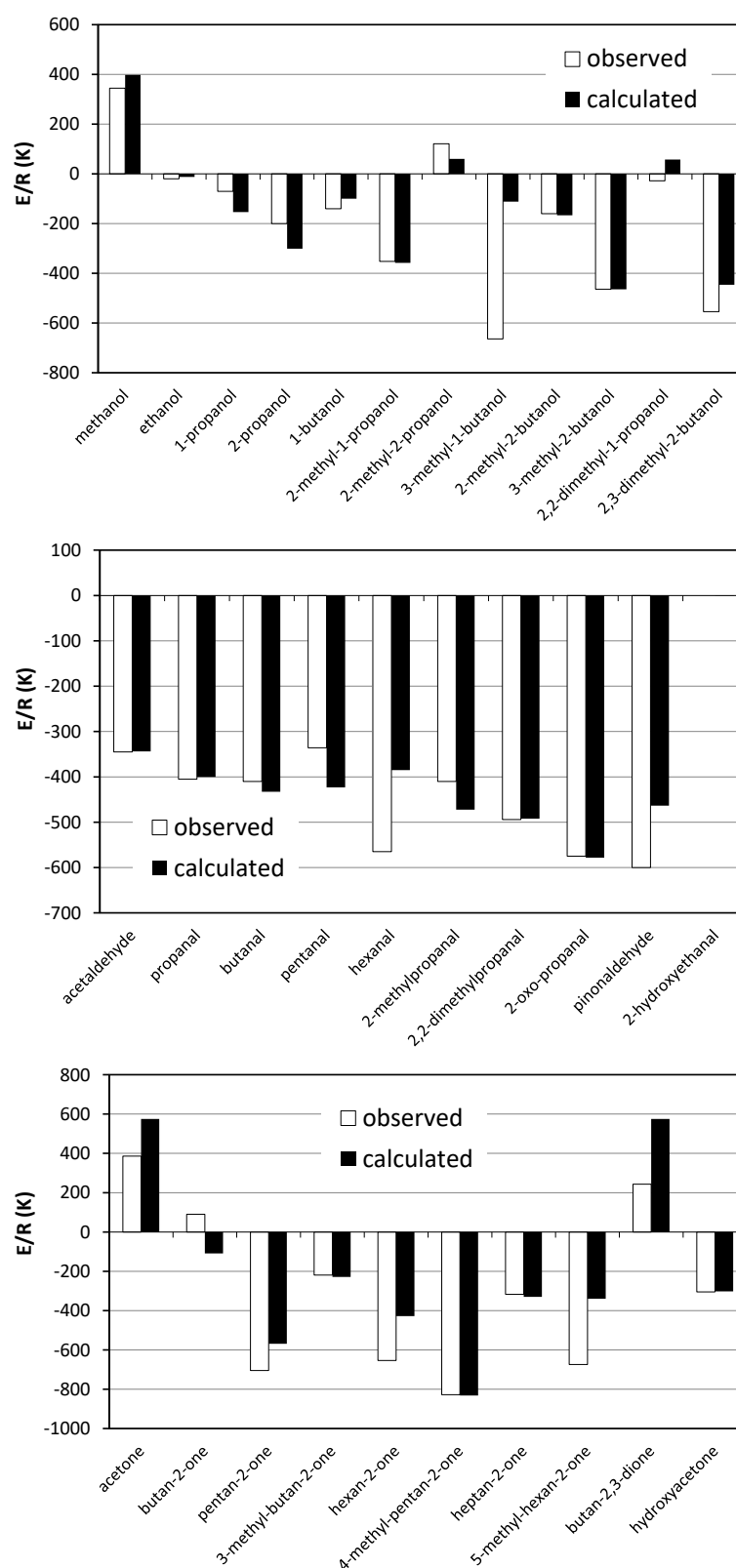


Figure S2. Comparison of observed (recommended) temperature coefficients (E/R) for the reactions of OH with 32 saturated compounds containing combinations of carbonyl and hydroxy groups, compared with those estimated in the present work. The upper panel shows data for monoalcohols, the middle panel for aldehydes, ketoaldehydes and hydroxyaldehydes, and the lower panel for ketones, diketones and hydroxyketones. In the case of 2-hydroxyethanal (glycolaldehyde), $(E/R)_{\text{obs}} = 0$ and $(E/R)_{\text{calc}} = 0.6$ K.

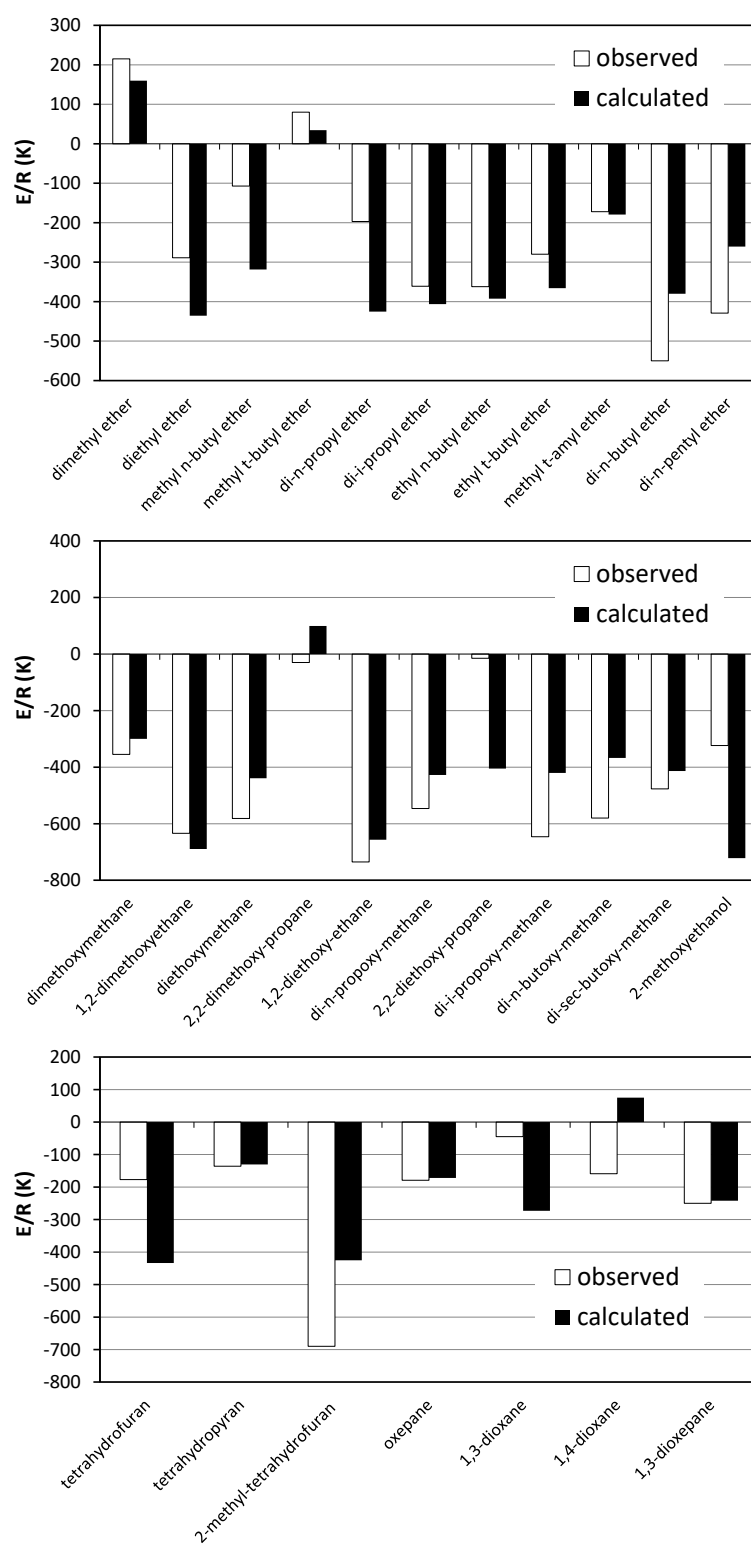


Figure S3. Comparison of observed (recommended) temperature coefficients (E/R) for the reactions of OH with 22 saturated acyclic ethers and 7 cyclic ethers, compared with those estimated in the present work. The upper panel shows data for monoethers, the middle panel for diethers and hydroxyethers, and the lower panel for cyclic ethers and diethers.

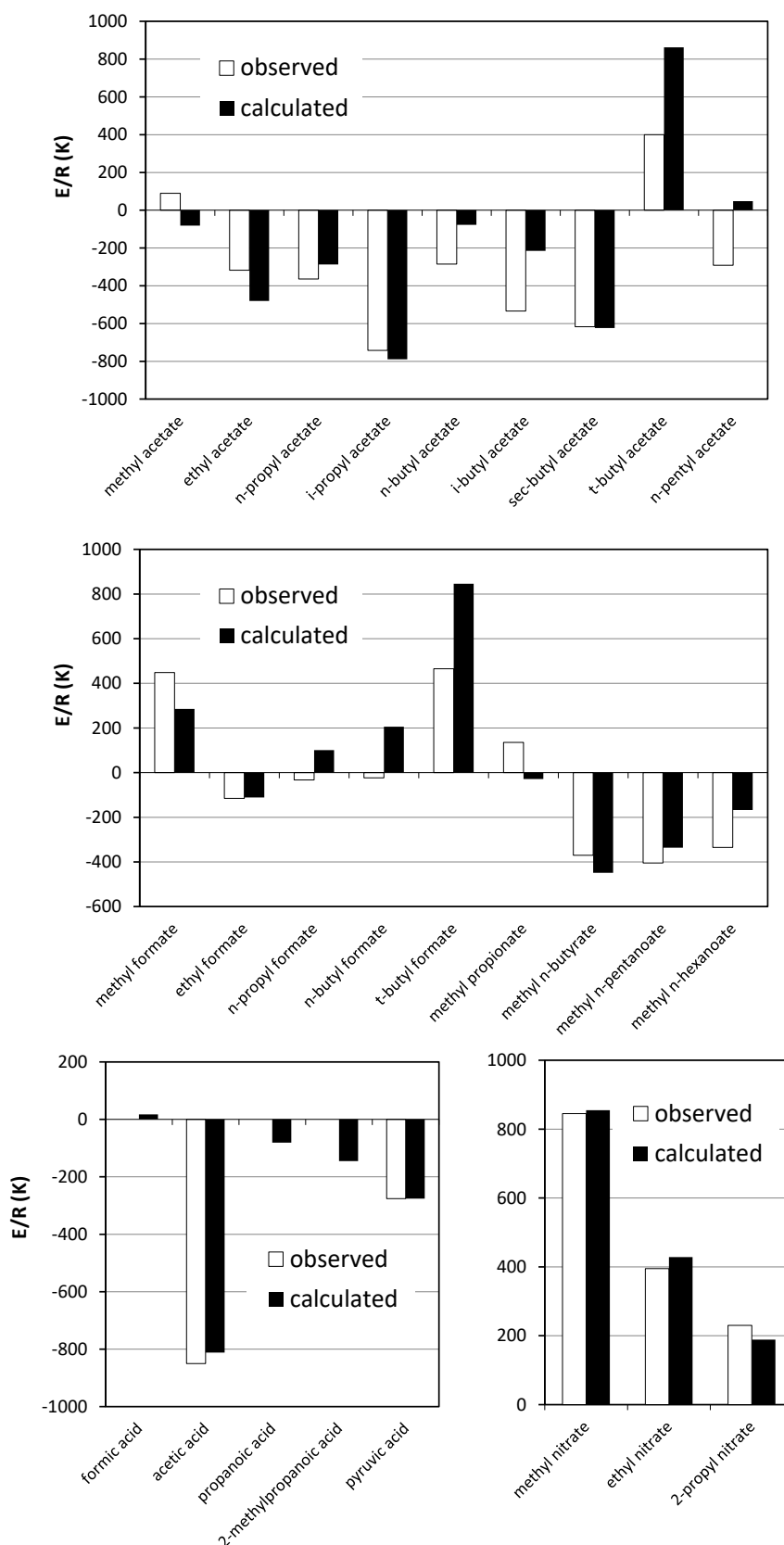


Figure S4. Comparison of observed (recommended) temperature coefficients (E/R) for the reactions of OH with 18 saturated esters, 5 carboxylic acids and 3 alkyl nitrates. The upper panel shows data for acetate esters, the middle panel for formate esters and higher esters, and the lower panels for carboxylic acids and alkyl nitrates.

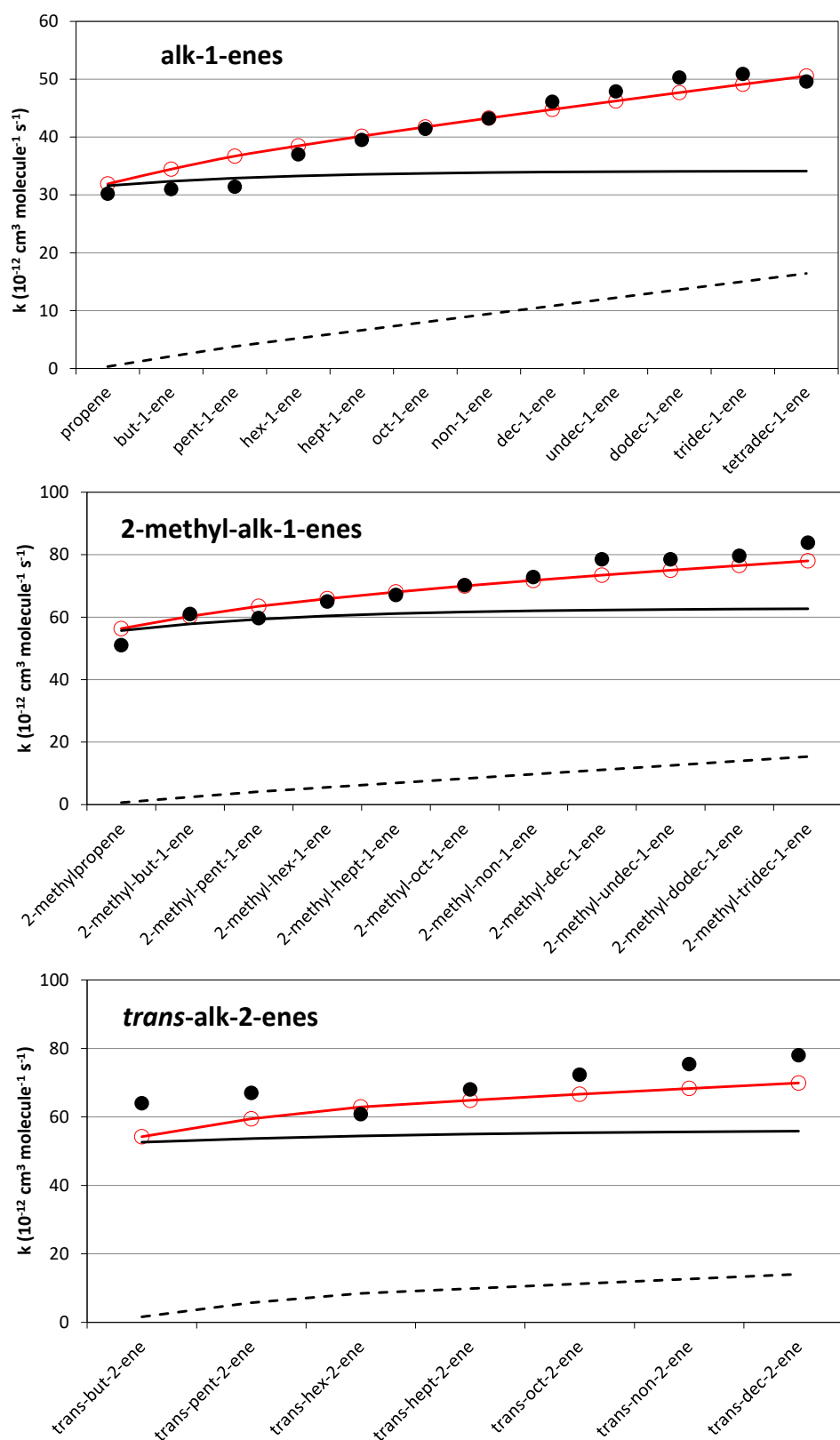


Figure S5. Comparison of observed (recommended) rate coefficients (filled black points) and calculated rate coefficients (open red points) at 298 K for homologous series of alk-1-enes, 2-methyl-alk-1-enes and *trans*-alk-2-enes. In each case, the continuous black line shows the calculated variation of k_{add} , and the broken black line the calculated variation of k_{abs} .

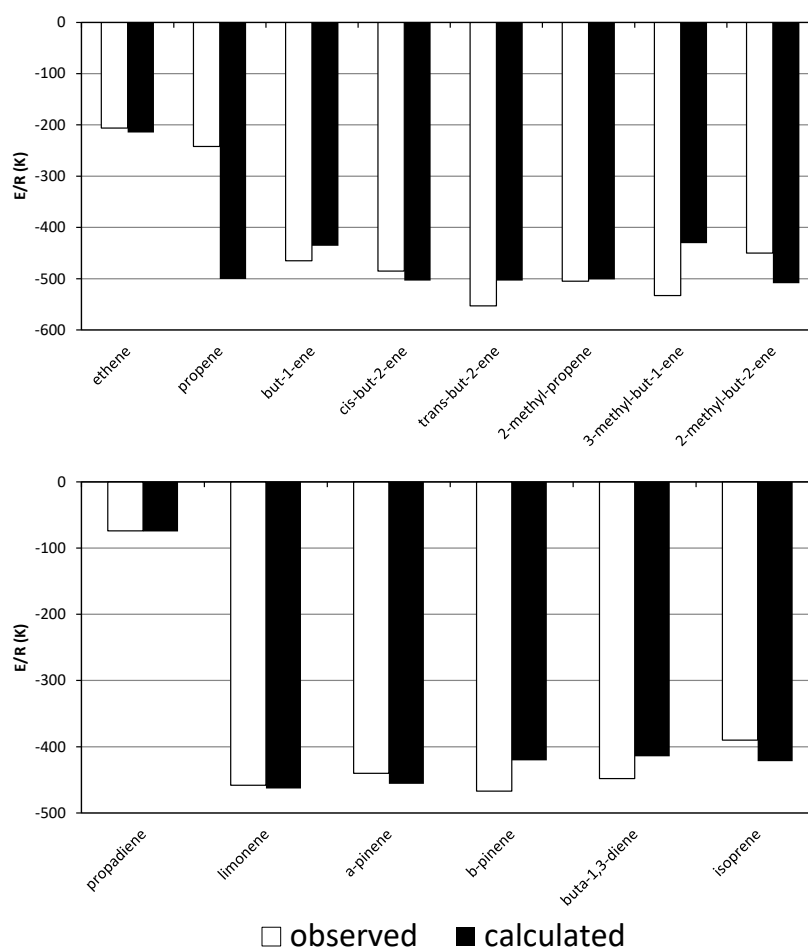


Figure S6. Comparison of observed (recommended) temperature coefficients (E/R) for the reactions of OH with alkenes and polyalkenes, compared with those estimated in the present work. The upper panel shows data for 8 acyclic monoalkenes, and the lower panel data for other alkenes and dialkenes for which temperature-dependence recommendations are available.

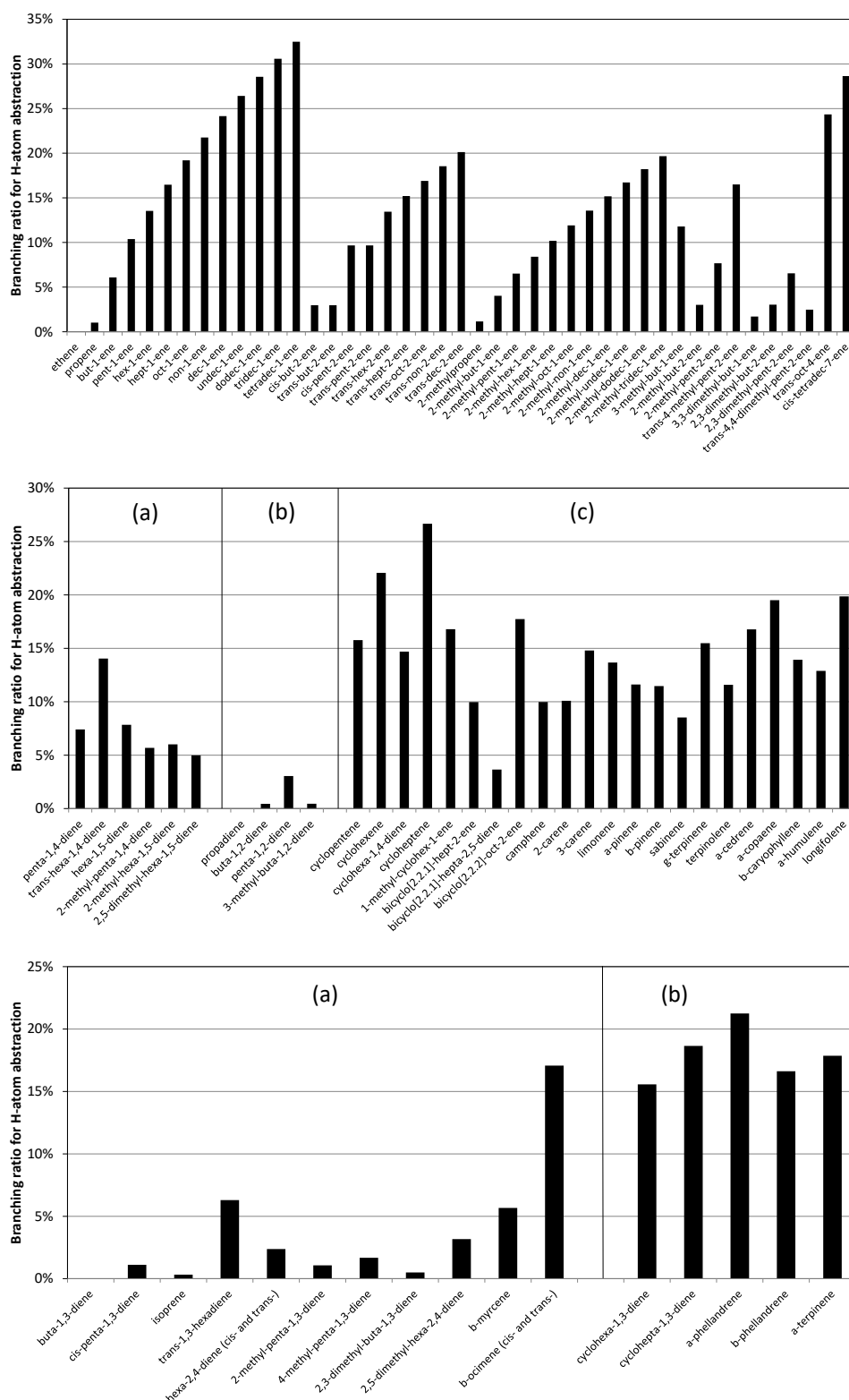


Figure S7. Estimated 298 K total branching ratios for H-atom abstraction, $k_{\text{abs}}/(k_{\text{abs}} + k_{\text{add}})$, in the reactions of OH with alkenes. **Upper panel:** 43 acyclic monoalkenes. **Middle panel:** (a) 6 acyclic unconjugated (isolated) dienes; (b) 4 acyclic cumulated dienes; (c) 22 cyclic alkenes and cyclic unconjugated (isolated) dienes. **Lower panel:** (a) 11 acyclic conjugated dialkenes; (b) 5 cyclic conjugated dialkenes.

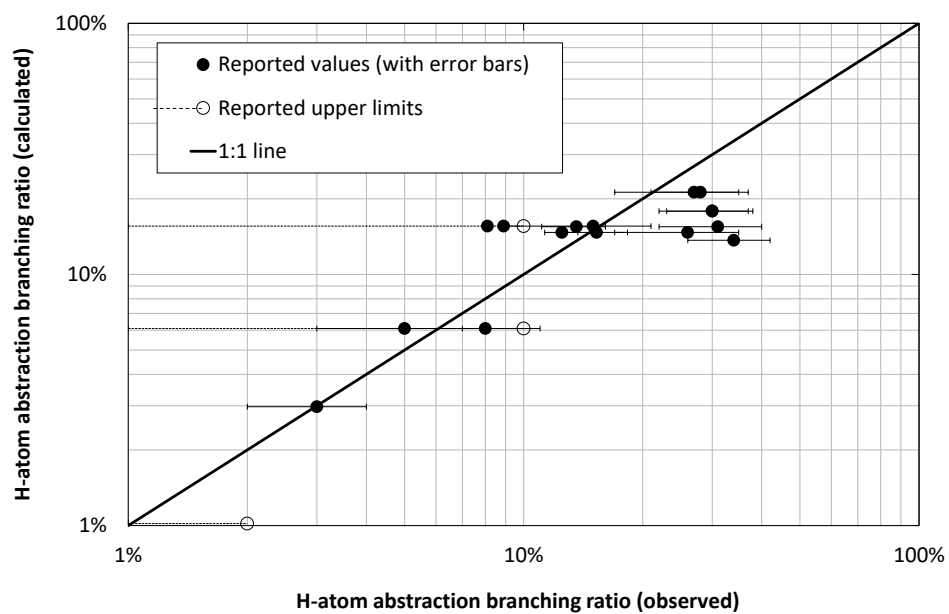


Figure S8. Comparison of 298 K estimated total branching ratios for H-atom abstraction, $k_{\text{abs}}/(k_{\text{abs}} + k_{\text{add}})$, with observed values reported in the literature, as listed in Table 13 of the main paper.

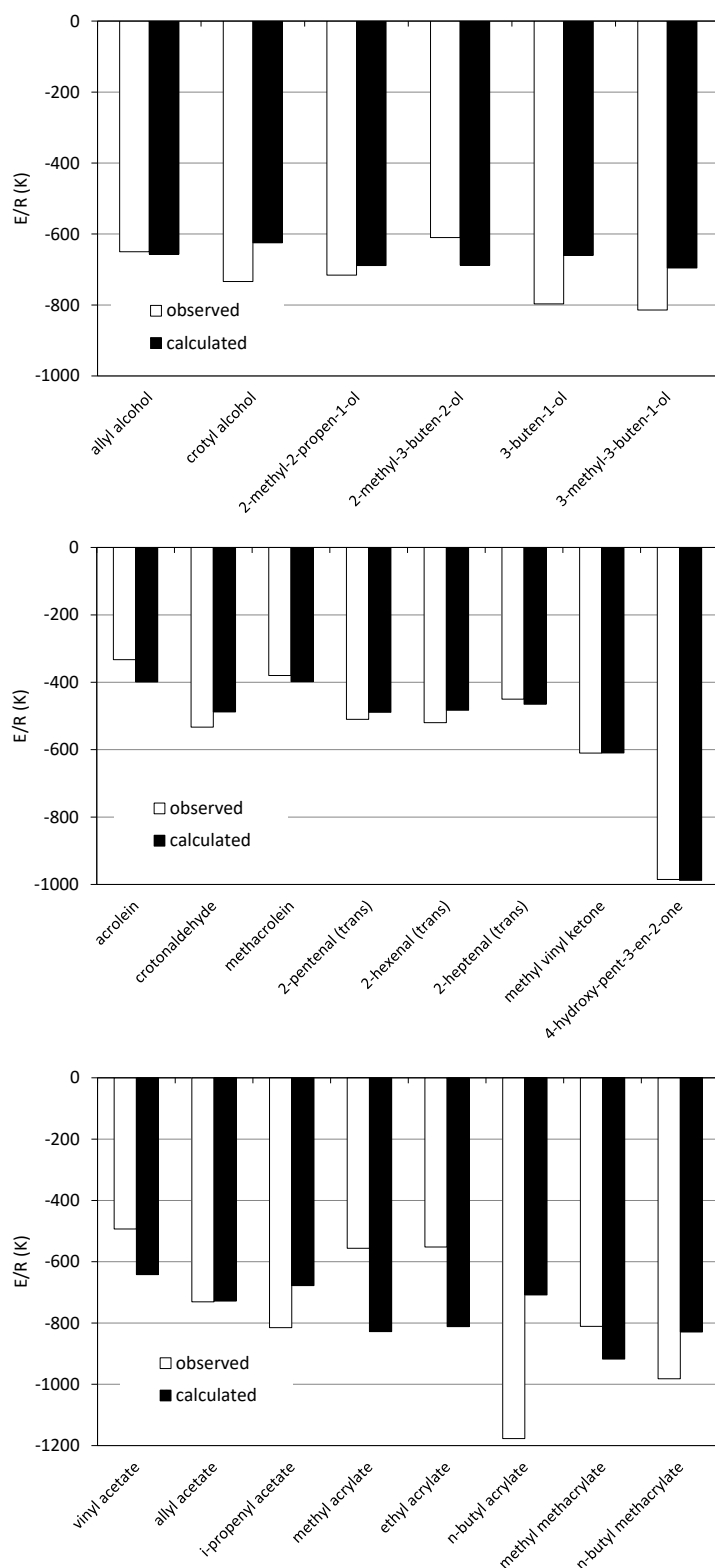


Figure S9. Comparison of observed (recommended) temperature coefficients (E/R) for the reactions of OH with unsaturated organic oxygenates, compared with those estimated in the present work. The upper panel shows data for 6 alcohols, the middle panel for 6 aldehydes, one ketone and one hydroxyketone, and the lower panel data for 8 esters for which temperature-dependence recommendations are available.

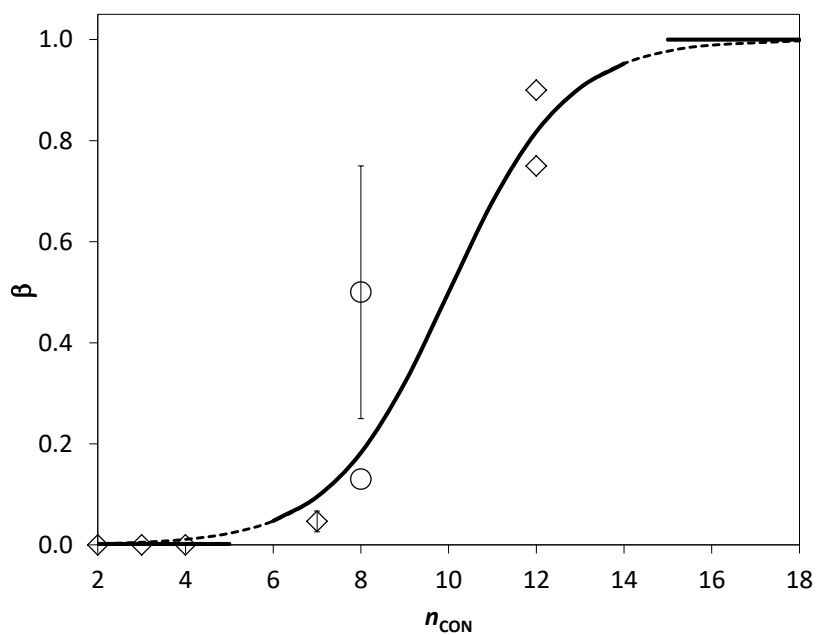


Figure S10. Reported fractional formation of thermalized α -hydroxy peroxy radicals (β), presented as a function of n_{CON} . Open circles are laboratory determinations; open diamonds are theoretical determinations (see Sect. 6.2 and Table 16 of the main paper). The curve is a sigmoid function, $\beta = [1 + \exp(-0.75(n_{\text{CON}} - 10))]^{-1}$, providing an approximate representation of the reported data.

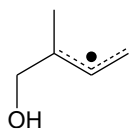
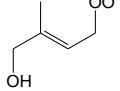
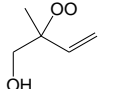
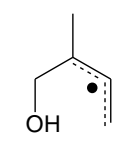
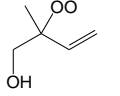
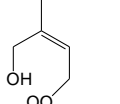
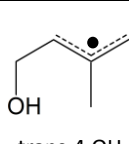
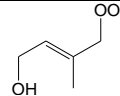
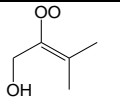
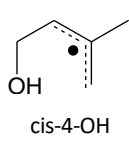
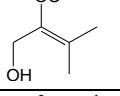
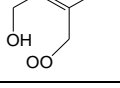
Table S1. Identities of outliers, where k_{calc} and k_{obs} at 298 K differ by more than a factor of two.

Systematic name	Alternative name	$k_{\text{calc}}/k_{\text{obs}}$	Compound class ^a
tetracyclo[2.2.1.0 ^{2,6} .0 ^{3,5}]heptane	quadricyclane	0.469	poly-cycloalkanes (Fig. 1)
butan-1,4-diol		0.364	di-alcohols (Fig. 2, Sect. 3.2.1)
6,6-dimethyl-bicyclo[3.1.1]heptan-2-one	nopinone	0.257	cycloketones (Fig. 2, Sect. 3.2.1)
[2,2-dimethyl-3-(2-oxo-propyl)-cyclopropyl]-acetaldehyde	caronaldehyde	0.474	keto-/di-aldehydes (Fig. 2, Sect. 3.2.1)
di-i-propoxy-methane		0.490	acyclic diethers (Fig. 3, Sect. 3.2.3)
methanoic acid 2-methanaloxy-ethyl ester	ethylene glycol diformate	3.98	di-esters (Fig. 4, Sect. 3.2.4)
ethanoic acid 2-ethanaloxy-ethyl ester	ethylene glycol diacetate	2.16	di-esters (Fig. 4, Sect. 3.2.4)
pentandioic acid dimethyl ester	dimethyl glutarate	2.17	di-esters (Fig. 4, Sect. 3.2.4)
1,2-dinitrooxybutane		0.361	acyclic alkyl dinitrates (Fig. 5, Sect. 3.2.5)
2,3-dinitrooxybutane		0.246	acyclic alkyl dinitrates (Fig. 5, Sect. 3.2.5)
1,4-dinitrooxybutane		0.165	acyclic alkyl dinitrates (Fig. 5, Sect. 3.2.5)
2-nitrooxy-1-propanol		0.264	acyclic hydroxynitrates (Fig. 5, Sect. 3.2.5)
2-nitrooxy-1-butanol		0.323	acyclic hydroxynitrates (Fig. 5, Sect. 3.2.5)
3-nitrooxy-1-butanol		0.416	acyclic hydroxynitrates (Fig. 5, Sect. 3.2.5)
5-nitrooxy-2-pentanol		0.344	acyclic hydroxynitrates (Fig. 5, Sect. 3.2.5)
4-nitrooxy-1-pentanol		0.259	acyclic hydroxynitrates (Fig. 5, Sect. 3.2.5)
6-nitrooxy-1-hexanol		0.324	acyclic hydroxynitrates (Fig. 5, Sect. 3.2.5)
3-methyl-cyclohex-2-enone		2.53	α,β -unsaturated ketones (Fig. 7, Table 11)
3,5,5-trimethyl-cyclohex-2-enone		3.15	α,β -unsaturated ketones (Fig. 7, Table 11)
cis-3-hexene-2,5-dione		0.442	α,β -unsaturated ketones (Fig. 7, Table 11)
3,4-dihydroxy-3-hexene-2,5-dione		0.322	α,β -unsaturated keto-enols (Fig. 7, Table 11)
4-nitrooxy-but-2-en-1-ol		2.83	hydroxyalkenyl nitrates (Fig. 7)
Comments ^a Class assigned to given compound in the identified figure. Where relevant, additional information and/or discussion is provided in the section or table shown.			

Table S2. Prompt rearrangements of chemically activated β -hydroxy-organic radicals formed from addition of OH to C=C bonds containing specific substituents.

Reaction	Comment	Reaction	Comment	Reaction	Comment
 	<p>(a)</p> <p>(b)</p> <p>(c)</p>	 	<p>(d)</p> <p>(e)</p>	 	<p>(f)</p> <p>(g)</p>
<p>Comments</p> <p>^a Reaction can proceed via breaking of either of two C-C bonds in the cyclopropyl ring. The reaction is assumed to proceed 50 % via each route. The corresponding thermalized cyclopropyl-β-hydroxyalkyl radicals formed via other routes (e.g. decomposition of larger oxy radicals) react as shown in Table 14 of the main paper (see also note (f) in Table 14);</p> <p>^b The corresponding thermalized oxiranyl-β-hydroxyalkyl radicals formed via other routes (e.g. decomposition of larger oxy radicals) react as shown in Table 14 of the main paper (see also note (f) in Table 14);</p> <p>^c Based on the calculations of Vereecken and Peeters (2000) for the relevant β-hydroxy-organic radical formed from the reaction of OH with α-pinene. The corresponding thermalized gem-disubstituted cyclobutyl-β-hydroxyalkyl radicals formed via other routes (e.g. decomposition of larger oxy radicals) are assumed to react exclusively with O₂ via reaction (R1) under atmospheric conditions;</p> <p>^d Based on the calculations of Greenwald et al. (2005) and Greenwald et al. (2010) for the relevant unsaturated β-hydroxy-organic radicals formed from the reactions of OH with buta-1,3-diene and isoprene. The branching ratios for R' = alkyl are also adopted for organic groups containing other substituents. The corresponding thermalized unsaturated β-hydroxy-organic radicals formed via other routes (e.g. decomposition of larger oxy radicals) are assumed to react exclusively with O₂ via reaction (R1) under atmospheric conditions;</p> <p>^e Based on the observations and calculations of Paulot et al. (2009), Bates et al. (2014) and St. Clair et al. (2016) for the reactions of OH with α,β-unsaturated hydroperoxides formed from the OH-initiated oxidation of isoprene (N.B. if there is a conflict, the rules in notes (a)-(c) above take precedence over this rule to avoid formation of strained bicyclic structures). The corresponding thermalized organic radicals formed via other routes are assumed to react exclusively with O₂ via reaction (R1) under atmospheric conditions;</p> <p>^f Based on the observations and calculations of Kjaergaard et al. (2012) for the reactions of OH with peroxymethacrylic acid and peroxyacrylic acid. The corresponding thermalized organic radicals formed via other routes are assumed to react exclusively with O₂ via reaction (R1) under atmospheric conditions;</p> <p>^g Based on the observations and calculations of Kjaergaard et al. (2012) and Nguyen et al. (2015) for the reactions of OH with peroxymethacryloyl nitrate (MPAN) and peroxyacryloyl nitrate (APAN). The corresponding thermalized organic radicals formed via other routes are assumed to react exclusively with O₂ via reaction (R1) under atmospheric conditions.</p>					

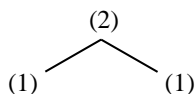
Table S3. Preferred partial rate coefficients for the addition of O₂ to hydroxy-substituted allyl radicals formed from the addition of OH to isoprene, and for the reverse decomposition of the hydroxy-allyl peroxy radicals formed.^a

Reagent	Product	A _f	(E/R) _f	k _{f, 298 K}	A _r	(E/R) _r	k _{r, 298 K}
		Forward reaction			Reverse reaction		
		10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹	K	10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹	10 ¹⁴ s ⁻¹	K	s ⁻¹
 trans-1-OH	 E-1-OH-4-OO	2.5	480	0.50	2.86	9028	19.9
	 1-OH-2-OO	3.0	0	3.0	85.5	10743	1.89
 cis-1-OH	 1-OH-2-OO	3.0	0	3.0	86.2	11322	0.272
	 Z-1-OH-4-OO	3.5	0	3.5	52.2	9838	24.0
 trans-4-OH	 E-4-OH-1-OO	2.5	480	0.50	2.13	9984	0.600
	 4-OH-3-OO	3.5	0	3.5	105	11569	0.145
 cis-4-OH	 4-OH-3-OO	3.5	0	3.5	105	11705	0.0918
	 Z-4-OH-1-OO	2.0	0	2.0	30.6	10254	3.48
Comments: ^a As recommended by Peeters (2015), the kinetic parameters applied to both the O ₂ addition reactions and the peroxy radical back decomposition reactions are based on those calculated by Peeters et al. (2014), but with each increased by a factor of 5 on the basis of the experimental characterization of the equilibration of peroxy radicals in each subset, as reported in preliminary form by Crounse et al. (2014) and applied in MCM v3.3.1; see Jenkin et al. (2015) for further details. The names assigned to the radical intermediates are taken from Peeters et al. (2009).							

S2 SAR application examples for 298 K

Calculated rate coefficients and branching ratios at 298 K are presented for selected example VOCs.

Example A: propane



Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$(1) k_{\text{prim}} \times F(-\text{CH}_2-) = 0.13 \times 1.35 \times 2 = \mathbf{0.351}$$

$$(2) k_{\text{sec}} \times F(-\text{CH}_3)^2 = 0.769 \times 1.0 \times 1.0 = \mathbf{0.769}$$

Total calculated rate coefficient: $1.12 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $1.10 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.313 (1): 0.687 (2)

Allowing for minor formation of nitrate products, the above distribution results in the following calculated yields of major products when $\text{RO}_2 + \text{NO}$ reaction dominates:

$\text{CH}_3\text{C}(\text{O})\text{CH}_3$ (acetone): 65.8 % (via route (2))

$\text{C}_2\text{H}_5\text{CHO}$ (propanal): 30.5 % (via route (1))

Attack distributions reported in experimental studies:

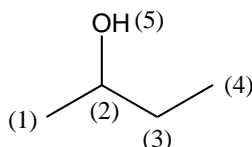
Droege and Tully (1986): 0.28 (1): 0.72 (2)

Reported yields of major products in experimental study:

Cox et al. (1980)

$\text{CH}_3\text{C}(\text{O})\text{CH}_3$ (acetone): 56 %

Example B: butan-2-ol



Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$(1) k_{\text{prim}} \times F(-\text{CH}(\text{OH})-) = 0.13 \times 2.7 = \mathbf{0.351}$$

$$(2) k_{\text{tert}} \times F(-\text{OH}) \times F(-\text{CH}_2-) \times F(-\text{CH}_3) = 1.49 \times 3.6 \times 1.35 \times 1.0 = \mathbf{7.241}$$

$$(3) k_{\text{sec}} \times F(-\text{CH}(\text{OH})-) \times F(-\text{CH}_3) = 0.769 \times 2.7 \times 1.0 = \mathbf{2.076}$$

$$(4) k_{\text{prim}} \times F(-\text{CH}_2-) = 0.13 \times 1.35 = \mathbf{0.176}$$

$$(5) k_{\text{abs}(-\text{OH})} = \mathbf{0.140}$$

Total calculated rate coefficient: $9.98 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $8.70 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.035 (1): 0.725 (2): 0.208 (3): 0.018 (4): 0.014 (5)

The above distribution results in the following calculated major product yield:

$\text{C}_2\text{H}_5\text{C}(\text{O})\text{CH}_3$ (butan-2-one): 72.5 % (via route (2))

Reported yields of major products in experimental study:

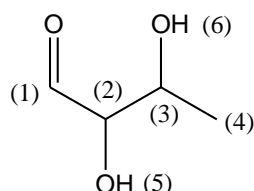
Chew and Atkinson (1996)

C₂H₅C(O)CH₃ (butan-2-one): (70 ± 7) %

Baxley and Wells (1998)

C₂H₅C(O)CH₃ (butan-2-one): (60 ± 2) %

Example C: 2,3-dihydroxybutanal



Partial rate coefficients (in units 10⁻¹² cm³ molecule⁻¹ s⁻¹):

(1) $k_{\text{abs(-CHO)st-}\alpha\text{O}} = \mathbf{12.700}$

(2) $k_{\text{tert}} \times F(\text{-C=O-}) \times F(\text{-OH}) \times F(\text{-CH(OH)-}) = 1.49 \times 1.0 \times 3.6 \times 2.7 = \mathbf{14.483}$

(3) $k_{\text{tert}} \times F(\text{-OH}) \times (F(\text{-CH(OH)-}) \times F(\text{-CH(C(=O)-)})^{\frac{1}{2}} \times F(\text{-CH}_3)) = 1.49 \times 3.6 \times (2.7 \times 3.4)^{\frac{1}{2}} \times 1.0 = \mathbf{16.252}$

(4) $k_{\text{prim}} \times F(\text{-CH(OH)-}) = 0.13 \times 2.7 = \mathbf{0.351}$

(5) $k_{\text{abs(-OH)}} = \mathbf{0.140}$

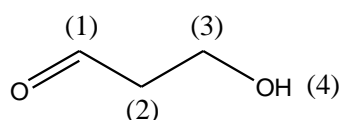
(6) $k_{\text{abs(-OH)}} = \mathbf{0.140}$

Total calculated rate coefficient: $4.41 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $4.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.288 (1): 0.329 (2): 0.369 (3): 0.008 (4): 0.003 (5): 0.003 (6)

Example D: 3-hydroxypropanal



(1) $k_{\text{abs(-CHO)-}\beta\text{OH}} = \mathbf{9.000}$

(2) $k_{\text{sec}} \times F(\text{-C=O-}) \times F(\text{-CH}_2\text{OH}) = 0.769 \times 1.0 \times 2.7 = \mathbf{2.076}$

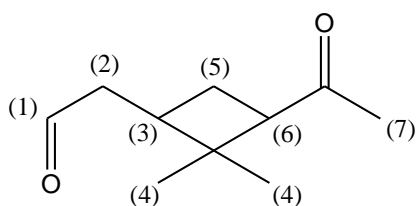
(3) $k_{\text{sec}} \times F(\text{-OH}) \times F(\text{-CH}_2\text{C(=O)-}) = 0.769 \times 3.6 \times 3.4 = \mathbf{9.413}$

(5) $k_{\text{abs(-OH)}} = \mathbf{0.140}$

Total calculated rate coefficient: $2.06 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $1.99 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.436 (1): 0.101 (2): 0.456 (3): 0.007 (4)

Example E: pinonaldehyde ((3-acetyl-2,2-dimethyl-cyclobutyl)-acetaldehyde)

Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

(1) $k_{\text{abs(-CHO)}} = \mathbf{20.800}$

(2) $k_{\text{sec}} \times F(-\text{C(=O)-}) \times F(-\text{CH<}) = 0.769 \times 1.0 \times 1.35 = \mathbf{1.038}$

(3) $k_{\text{tert}} \times F(-\text{CH(C(=O))-}) \times F(-\text{CH}_2-) \times F(>\text{C<}) \times F_{\text{ring}}(4) = 1.49 \times 3.4 \times 1.35 \times 1.35 \times 0.41 = \mathbf{3.785}$

(4) $k_{\text{prim}} \times F(>\text{C<}) \times 2 = 0.13 \times 1.35 \times 2 = \mathbf{0.351}$

(5) $k_{\text{sec}} \times F(-\text{CH(C(=O))-}) \times F(-\text{CH<}) \times F_{\text{ring}}(4) = 0.769 \times 3.4 \times 1.35 \times 0.41 = \mathbf{1.447}$

(6) $k_{\text{tert}} \times F(-\text{C(=O)-}) \times F(-\text{CH}_2-) \times F(>\text{C<}) \times F_{\text{ring}}(4) = 1.49 \times 1.0 \times 1.35 \times 1.35 \times 0.41 = \mathbf{1.113}$

(7) $k_{\text{prim}} \times F(-\text{C(=O)-}) = 0.13 \times 1.0 = \mathbf{0.130}$

Total calculated rate coefficient: $2.87 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $3.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.726 (1): 0.036 (2): 0.132 (3): 0.012 (4): 0.050 (5): 0.039 (6): 0.005 (7)

Attack distributions reported in theoretical studies:

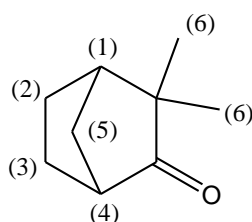
Fantechi et al. (2002): 0.590 (1): 0.230 (2): 0.085 (3): 0.023 (4): 0.010 (5): 0.057 (6): – (7)

Dash and Rajakumar (2012):

(a) Wigner: 0.605 (1): 0.098 (2): 0.065 (3): 0.041 (4): 0.058 (5): 0.130 (6): – (7)

(b) Eckhart symmetrical: 0.591 (1): 0.114 (2): 0.065 (3): 0.048 (4): 0.062 (5): 0.120 (6): – (7)

(c) Eckhart unsymmetrical: 0.555 (1): 0.043 (2): 0.134 (3): 0.027 (4): 0.036 (5): 0.200 (6): – (7)

Example F: camphenilone (3,3-dimethyl-bicyclo[2.2.1]heptan-2-one)

Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

(1) $k_{\text{tert}} \times F(-\text{C(C(=O))-<}) \times F(-\text{CH}_2-) \times F(-\text{CH}_2-) \times F_{\text{ring}}(5) \times F_{\text{ring-CO}}(5) \times F_{\text{ring-CO}}(6) = 1.49 \times 3.4 \times 1.35 \times 1.35 \times 0.69 \times 0.32 \times 0.61 = \mathbf{1.244}$

(2) $k_{\text{sec}} \times F(-\text{CH}_2-) \times F(-\text{CH<}) \times F_{\text{ring}}(5) \times F_{\text{ring-CO}}(6) = 0.769 \times 1.35 \times 1.35 \times 0.69 \times 0.61 = \mathbf{0.590}$

(3) $k_{\text{sec}} \times F(-\text{CH}_2-) \times F(-\text{CH(C(=O))-<}) \times F_{\text{ring}}(5) \times F_{\text{ring-CO}}(6) = 0.769 \times 1.35 \times 3.4 \times 0.69 \times 0.61 = \mathbf{1.486}$

(4) $k_{\text{tert}} \times F(-\text{C(=O)-}) \times F(-\text{CH}_2-) \times F(-\text{CH}_2-) \times F_{\text{ring}}(5) \times F_{\text{ring-CO}}(5) \times F_{\text{ring-CO}}(6) = 1.49 \times 1.0 \times 1.35 \times 1.35 \times 0.69 \times 0.32 \times 0.61 = \mathbf{0.366}$

(5) $k_{\text{sec}} \times F(-\text{CH<}) \times F(-\text{CH(C(=O))-<}) \times F_{\text{ring}}(5) \times F_{\text{ring-CO}}(5) = 0.769 \times 1.35 \times 3.4 \times 0.69 \times 0.32 = \mathbf{0.780}$

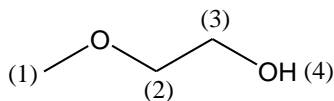
$$(6) k_{\text{prim}} \times F(-C(C(=O)-)<) \times 2 = 0.13 \times 3.4 \times 2 = \mathbf{0.884}$$

Total calculated rate coefficient: $5.35 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $4.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.233 (1): 0.110 (2): 0.278 (3): 0.068 (4): 0.146 (5): 0.165 (6)

Example G: 2-methoxyethanol



Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

(1) $k_{\text{abs(-OCH}_3\text{)}} = \mathbf{1.300}$

(2) $k_{\text{abs(-OR)}} = \mathbf{5.600}$

(3) $k_{\text{sec}} \times F(-OH) \times F(-CH_2OR) = 0.769 \times 3.6 \times 3.5 = \mathbf{9.689}$

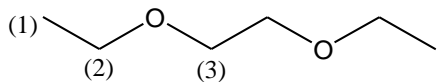
(4) $k_{\text{abs(-OH)}} = \mathbf{0.140}$

Total calculated rate coefficient: $1.67 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.078 (1): 0.335 (2): 0.579 (3): 0.008 (4): 0.008 (5)

Example H: 1,2-diethoxyethane



Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

(1) $k_{\text{prim}} \times F(-CH_2OR) \times 2 = 0.13 \times 3.5 \times 2 = \mathbf{0.910}$

(2) $k_{\text{abs(-OR)}} \times 2 = 5.6 \times 2 = \mathbf{11.200}$

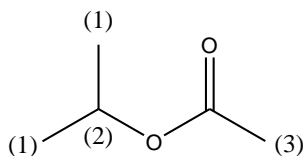
(3) $k_{\text{abs(-OCCOR)}} \times 2 = 15.0 \times 2 = \mathbf{30.000}$

Total calculated rate coefficient: $4.21 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.022 (1): 0.266 (2): 0.712 (3).

Example I: *i*-propyl acetate (ethanoic acid isopropyl ester)



Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

(1) $k_{\text{prim}} \times F(-CH<) = 0.13 \times 1.35 \times 2 = \mathbf{0.351}$

(2) $k_{\text{tert}} \times F(-CH_3) \times F(-CH_3) \times F(-OC(=O)R) = 1.49 \times 1.0 \times 1.0 \times 2.2 = \mathbf{3.278}$

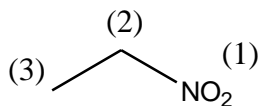
$$(3) k_{\text{prim}} \times F(-C(=O)OR) = 0.13 \times 0.4 = \mathbf{0.052}$$

$$\text{Total calculated rate coefficient: } 3.68 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\text{Preferred (observed) rate coefficient: } 3.79 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\text{Calculated attack distribution: } 0.095 (1): 0.891 (2): 0.014 (3)$$

Example J: nitroethane



Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$(1) k_{\text{add}(-\text{NO}_2)} = \mathbf{0.110}$$

$$(2) k_{\text{sec}} \times F(-\text{CH}_3) \times F(-\text{NO}_2) = 0.769 \times 1.0 \times 0.0 = \mathbf{0.0}$$

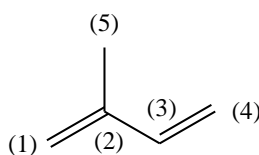
$$(3) k_{\text{prim}} \times F(-\text{CH}_2\text{NO}_2) = 0.13 \times 0.31 = \mathbf{0.040}$$

$$\text{Total calculated rate coefficient: } 1.50 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\text{Preferred (observed) rate coefficient: } 1.44 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\text{Calculated attack distribution: } 0.732 (1): 0.000 (2): 0.268 (3)$$

Example K: isoprene



Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$(1) k_{\text{tert,prim}} = \mathbf{61.000}$$

$$(2) k_{\text{prim-add}} = \mathbf{4.200}$$

$$(3) k_{\text{prim-add}} = \mathbf{4.200}$$

$$(4) k_{\text{sec,prim}} = \mathbf{30.000}$$

$$(5) k_{\text{prim}} \times F(-C=\text{CH}_2) = 0.13 \times 2.5 = \mathbf{0.325}$$

$$\text{Total calculated rate coefficient: } 9.97 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\text{Preferred (observed) rate coefficient: } 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

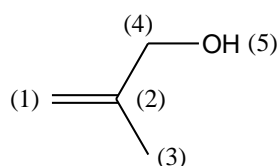
$$\text{Calculated attack distribution: } 0.612 (1): 0.042 (2): 0.042 (3): 0.301 (4): 0.003 (5)$$

Attack distributions reported in theoretical studies:

$$\text{McGivern et al. (2000): } 0.560 (1): 0.023 (2): 0.046 (3): 0.370 (4): - (5)$$

$$\text{Greenwald et al. (2007): } 0.670 (1): 0.020 (2): 0.020 (3): 0.290 (4): - (5)$$

Example L: 2-methyl-prop-2-en-1-ol



Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$(1) k_{\text{tert-add}} \times F'(-\text{CH}_2\text{OH}) = 51.5 \times 1.8 = \mathbf{92.700}$$

$$(2) k_{\text{prim-add}} = \mathbf{4.200}$$

$$(3) k_{\text{prim}} \times F(-\text{C}=\text{CH}_2) = 0.13 \times 2.5 = \mathbf{0.325}$$

$$(4) k_{\text{sec}} \times F(-\text{OH}) \times F(-\text{C}=\text{CH}_2) = 0.769 \times 3.6 \times 2.5 = \mathbf{6.921}$$

$$(5) k_{\text{abs(-OH)}} = \mathbf{0.140}$$

Total calculated rate coefficient: $1.04 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $9.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.889 (1): 0.040 (2): 0.003 (3): 0.066 (4): 0.001 (5)

Allowing for minor formation of nitrate products, the above distribution results in the following calculated yields of major products when $\text{RO}_2 + \text{NO}$ reaction dominates:

HCHO (formaldehyde): 88.7 % (via routes (1) and (2))

$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ (hydroxyacetone): 88.7 % (via routes (1) and (2))

$\text{CH}_2=\text{CH}(\text{CH}_3)\text{CHO}$ (methacrolein) : 6.8 % (via routes (4) and (5))

Reported yields of major products in experimental study:

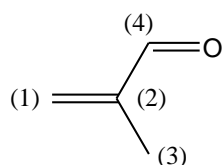
Peirone et al. (2014)

HCHO (formaldehyde): $(82 \pm 12) \%$

$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ (hydroxyacetone): $(84 \pm 13) \%$

$\text{CH}_2=\text{CH}(\text{CH}_3)\text{CHO}$ (methacrolein) : $(7.8 \pm 1.2) \%$

Example M: methacrolein (2-methyl-propenal)



Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$(1) k_{\text{tert-add}} \times F'(-\text{C}(=\text{O})\text{H}) = 51.5 \times 0.26 = \mathbf{13.390}$$

$$(2) k_{\text{prim-add}} = \mathbf{4.200}$$

$$(3) k_{\text{prim}} \times (F(-\text{C}=\text{CH}_2) \times F(-\text{C}(\text{C}(=\text{O})-\text{<)}))^{1/2} = 0.13 \times (2.5 \times 3.4)^{1/2} = \mathbf{0.379}$$

$$(4) k_{\text{abs(-CHO)-}\alpha\text{C}=\text{C}} = \mathbf{13.000}$$

Total calculated rate coefficient: $3.10 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

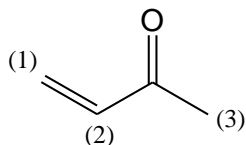
Preferred (observed) rate coefficient: $2.90 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.432 (1): 0.136 (2): 0.012 (3): 0.420 (4).

Attack distributions reported in experimental studies:

Chuong and Stevens (2004): 0.467 (1): 0.084 (2): – (3): 0.449 (4).

Example N: methylvinyl ketone (but-3-en-2-one)



Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$(1) k_{\text{sec-add}} \times F'(-\text{C}(=\text{O})-) = 26.3 \times 0.6 = \mathbf{15.780}$$

$$(2) k_{\text{prim-add}} = \mathbf{4.200}$$

$$(3) k_{\text{prim}} \times F(-\text{C}(=\text{O})-) = 0.13 \times 1.0 = \mathbf{0.130}$$

Total calculated rate coefficient: $2.01 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $2.00 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.785 (1): 0.209 (2): 0.007 (3).

Allowing for minor formation of nitrate products, the above distribution results in the following calculated yields of major products when $\text{RO}_2 + \text{NO}$ reaction dominates:

HOCH_2CHO (glycolaldehyde) : 73.1 % (via route (1))

$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ (hydroxyacetone): 19.4 % (via route (2))

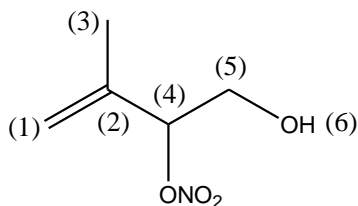
Reported yields of major products in experimental study:

Praske et al. (2015)

HOCH_2CHO (glycolaldehyde) : $(76 \pm 14) \%$

$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ (hydroxyacetone): $(24 \pm 14) \%$

Example O: 3-methyl-2-nitrooxybut-3-ene-1-ol



Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$(1) k_{\text{tert-add}} \times F'(-\text{CH}(\text{ONO}_2)-) \times F'(-\text{C}-\text{CH}_2\text{OH}) = 51.5 \times 0.26 \times 1.8 = \mathbf{24.102}$$

$$(2) k_{\text{prim-add}} = \mathbf{4.200}$$

$$(3) k_{\text{prim}} \times F(-\text{C}=\text{CH}_2) = 0.13 \times 2.5 = \mathbf{0.325}$$

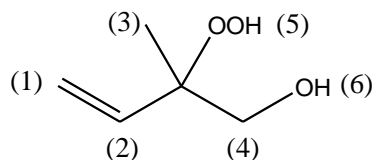
$$(4) k_{\text{tert}} \times F(-\text{C}=\text{CH}_2) \times F(-\text{ONO}_2) \times F(-\text{CH}_2\text{OH}) = 1.49 \times 2.5 \times 0.16 \times 2.7 = \mathbf{1.609}$$

$$(5) k_{\text{sec}} \times F(-\text{OH}) \times F(-\text{CH}(\text{NO}_2)-) = 0.769 \times 3.6 \times 0.34 = \mathbf{0.941}$$

$$(6) k_{\text{abs}(-\text{OH})} = \mathbf{0.140}$$

<u>Total calculated rate coefficient:</u>	$3.13 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
<u>Preferred (observed) rate coefficient:</u>	$3.90 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
<u>Calculated attack distribution:</u>	0.770 (1): 0.134 (2): 0.010 (3): 0.051 (4): 0.030 (5): 0.004 (6).

Example P: 2-hydroperoxy-2-methyl-but-3-en-1-ol



Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$(1) k_{\text{sec-add}} \times F'(-\text{C}(\text{OOH})<) \times F'(-\text{C}-\text{CH}_2\text{OH}) = 26.3 \times 1.2 \times 1.8 = \mathbf{56.808}$$

$$(2) k_{\text{prim-add}} = \mathbf{4.200}$$

$$(3) k_{\text{prim}} \times F(>\text{C}<) = 0.13 \times 1.35 = \mathbf{0.176}$$

$$(4) k_{\text{sec}} \times F(-\text{OH}) \times F(>\text{C}<) = 0.769 \times 3.6 \times 1.35 = \mathbf{3.737}$$

$$(5) k_{\text{abs}(-\text{OOH})} = \mathbf{3.100}$$

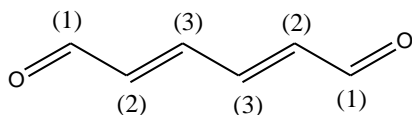
$$(6) k_{\text{abs}(-\text{OH})} = \mathbf{0.140}$$

$$\text{Total calculated rate coefficient: } 6.82 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\text{Preferred (observed) rate coefficient: } 8.30 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\text{Calculated attack distribution: } 0.833 (1): 0.062 (2): 0.003 (3): 0.055 (4): 0.045 (5): 0.002 (6).$$

Example Q: hexa-2,4-dienedial



Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$(1) k_{\text{abs}(-\text{CHO})-\alpha\text{C}=\text{C}} \times 2 = 13.0 \times 2 = \mathbf{26.000}$$

$$(2) k_{\text{sec,sec}} \times F'(-\text{C}(=\text{O})\text{H})^{\frac{1}{2}} \times 2 = 40.0 \times 0.26^{\frac{1}{2}} \times 2 = \mathbf{40.792}$$

$$(3) k_{\text{sec-add}} \times F'(-\text{C}(=\text{O})\text{H}) \times 2 = 26.0 \times 0.26 \times 2 = \mathbf{13.520}$$

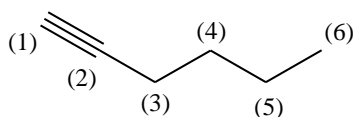
$$\text{Total calculated rate coefficient: } 8.03 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\text{Preferred (observed) rate coefficient: } 7.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (E,E-hexa-2,4-dienedial)}$$

$$7.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (E,Z-hexa-2,4-dienedial)}$$

$$\text{Calculated attack distribution: } 0.324 (1): 0.508 (2): 0.168 (3).$$

Example R: hex-1-yne



Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

Total addition rate coefficient, $k(\text{H-C}\equiv\text{C-R}) = k_{\text{C}\equiv\text{C}} \times F_{\text{C}\equiv\text{C}}(-\text{H}) \times F_{\text{C}\equiv\text{C}}(-\text{R}) = 0.94 \times 1.0 \times 8.0 = 7.52$

(1) $k(\text{H-C}\equiv\text{C-R}) \times (F_{\text{C}\equiv\text{C}}(-\text{R}) / (F_{\text{C}\equiv\text{C}}(-\text{H}) + F_{\text{C}\equiv\text{C}}(-\text{R}))) = 7.52 \times (8.0 / (1.0 + 8.0)) = \mathbf{6.684}$

(2) $k(\text{H-C}\equiv\text{C-R}) \times (F_{\text{C}\equiv\text{C}}(-\text{H}) / (F_{\text{C}\equiv\text{C}}(-\text{H}) + F_{\text{C}\equiv\text{C}}(-\text{R}))) = 7.52 \times (1.0 / (1.0 + 8.0)) = \mathbf{0.836}$

(3) $k_{\text{sec}} \times F(-\text{C}\equiv\text{C}-) \times F(-\text{CH}_2-) = 0.769 \times 1.0 \times 1.35 = \mathbf{1.038}$

(4) $k_{\text{sec}} \times F(-\text{CH}_2-) \times F(-\text{CH}_2-) = 0.769 \times 1.35 \times 1.35 = \mathbf{1.401}$

(5) $k_{\text{sec}} \times F(-\text{CH}_2-) \times F(-\text{CH}_3) = 0.769 \times 1.35 \times 1.0 = \mathbf{1.038}$

(6) $k_{\text{prim}} \times F(-\text{CH}_2-) = 0.13 \times 1.35 = \mathbf{0.176}$

Total calculated rate coefficient: $1.12 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $1.08 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.599 (1): 0.075 (2): 0.093 (3): 0.125 (4): 0.093 (5) 0.016 (6).

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