

Supplementary Material for:

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

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S1 Observed and estimated temperature coefficients

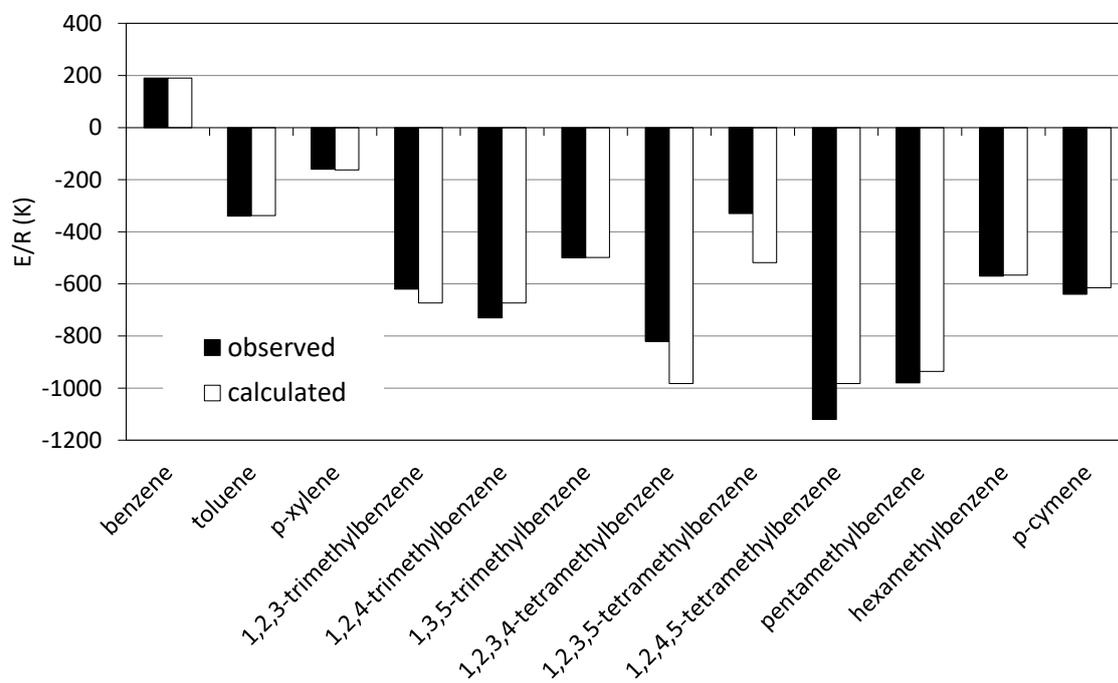


Figure S1. Comparison of observed (recommended) temperature coefficients (E/R) for the reactions of OH with benzene, 10 methyl-substituted aromatics and p-cymene, compared with those estimated or assigned in the present work.

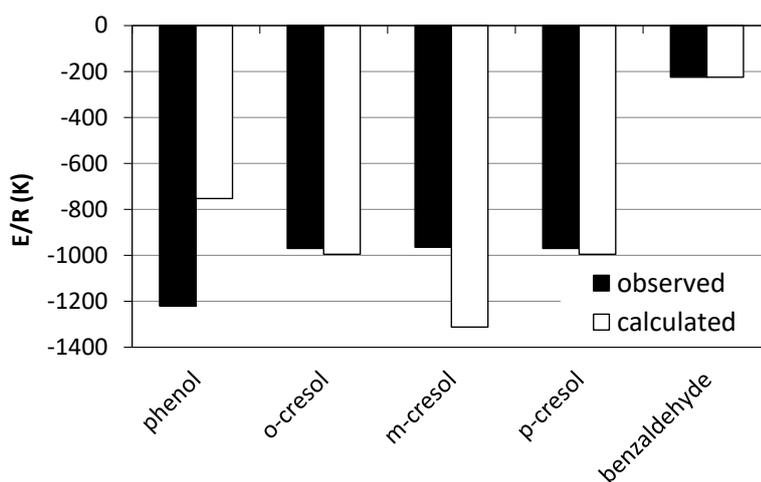


Figure S2. Comparison of observed (recommended) temperature coefficients (E/R) for the reactions of OH with phenol, cresols and benzaldehyde, compared with those estimated in the present work.

S2 Comparison of observed and calculated product yields

Tables S1 and S2 summarize observed and calculated yields of a number of reported first-generation end products and promptly-formed HO₂ radicals, from the OH-initiated oxidation of benzene and methyl-substituted aromatics. These data are also presented as a correlation plot in Fig. 5 of the main paper.

Table S1. Comparison of estimated and reported yields of hydroxyarene (phenolic) products at 298 K.

Compound	Product	Yield		Comment
		calculated	observed	
benzene	phenol	53.3 %	(54.2 ± 3.2) %	(a)
toluene	<i>o</i> -cresol	12.2 %	(12.2 ± 0.9) %	(b)
	<i>m</i> -cresol	3.7 %	(2.7 ± 0.4) %	
	<i>p</i> -cresol	3.3 %	(3.0 ± 0.3) %	
	total	19.2 %	(17.9 ± 1.6) %	
<i>m</i> -xylene	2,4-dimethyphenol	3.0 %	(6.0 ± 0.4) %	(c)
	2,6-dimethyphenol	5.8 %	(4.6 ± 0.3) %	
	3,5-dimethyphenol	1.8 %	(0.3 ± 0.03) %	
	total	10.6 %	(10.9 ± 0.7) %	
<i>p</i> -xylene	2,5-dimethyphenol	10.9 %	(13.0 ± 1.8) %	(c)
1,2,4-trimethylbenzene	2,3,6-trimethyphenol	2.4%	(1.4 ± 0.2) %	(c),(d)
	2,4,5-trimethyphenol	0.6%	(0.26 ± 0.04) %	
	2,3,5-trimethyphenol	0.8%	(0.5 ± 0.2) %	
	total	3.8 %	(2.2 ± 0.4) %	
1,3,5-trimethylbenzene	2,4,6-trimethyphenol	3.2 %	(4.0 ± 1.0) %	(c),(d)
Comments				
^a Observed value based on a weighted average of the yields reported by Volkamer et al. (2002), Berndt and Böge (2006) and Noda et al. (2009); ^b Observed values based on averages of the yields reported by Smith et al. (1998) and Klotz et al. (1998); ^c Observed values based on Smith et al. (1999); ^d Reported as tentative identification.				

Table S2. Comparison of estimated and reported yields of α -dicarbonyls, nitrates and prompt HO₂ at 298 K.

Compound	Product	Branching ratio		Comment
		calculated	observed	
benzene	glyoxal (and total α-dicarbonyl)	29.8 %	(35.0 ± 10.0) %	(a)
	nitrate	2.9 %	3.4 %	(b)
	HO ₂	67.3 %	(69 ± 10) %	(c)
toluene	glyoxal	25.4 %	(26.0 ± 2.2) %	(d)
	methylglyoxal	23.4 %	(21.5 ± 2.9) %	
	total α-dicarbonyl	48.8 %	(47.5 ± 5.1) %	
	nitrate	3.4 %	2.9 %	(b)
	HO ₂	41.5 %	(42 ± 11) %	(e)
<i>o</i> -xylene	glyoxal	19.0 %	(12.7 ± 1.9) %	(d),(f)
	methylglyoxal	22.4 %	(33.1 ± 6.1) %	
	biacetyl	15.1 %	(18.5 ± 2.8) %	
	total α-dicarbonyl	56.5 %	(64.3 ± 10.8) %	
	HO ₂	33.3 %	(41 ± 8) %	(e)

Table S2 (continued). Comparison of estimated and reported yields of α -dicarbonyls, nitrates and prompt HO₂ at 298 K.

Compound	Product	Branching ratio		Comment
		calculated	observed	
<i>m</i> -xylene	glyoxal	11.9 %	(11.4 ± 0.7) %	(d)
	methylglyoxal	45.7 %	(51.5 ± 8.5) %	
	total α-dicarbonyl	57.6 %	(62.9 ± 9.2) %	
	HO ₂	36.5 %	(27 ± 6) %	(e)
<i>p</i> -xylene	glyoxal	35.0 %	(38.9 ± 4.7) %	(d)
	methylglyoxal	19.1 %	(18.7 ± 2.2) %	
	total α-dicarbonyl	54.1 %	(57.6 ± 6.9) %	
	nitrate	2.5 %	2.5 %	(b)
	HO ₂	35.2 %	(40 ± 9) %	(e)
1,2,3-trimethylbenzene	glyoxal	4.7 %	(4.7 ± 2.4) %	(d),(f)
	methylglyoxal	24.5 %	(15.1 ± 3.3) %	
	biacetyl	34.0 %	(44.4 ± 5.3) %	
	total α-dicarbonyl	63.1 %	(64.2 ± 11.0) %	
		HO ₂	29.1 %	(31 ± 6) %
1,2,4-trimethylbenzene	glyoxal	13.2 %	(8.7 ± 1.6) %	(d),(f)
	methylglyoxal	32.3 %	(27.2 ± 8.1) %	
	biacetyl	15.6 %	(11.4 ± 2.4) %	
	total α-dicarbonyl	61.1 %	(47.3 ± 12.1) %	
		HO ₂	30.7 %	(37 ± 9) %
1,3,5-trimethylbenzene	methylglyoxal (and total α-dicarbonyl)	63.9 %	(58.1 ± 5.3) %	(d)
	nitrate	2.6 %	2.7 %	(g)
	HO ₂	31.7 %	(29 ± 8) %	(e)
hexamethylbenzene	biacetyl (and total α-dicarbonyl)	55.0 %	-	-
	HO ₂	28.0 %	(32 ± 8) %	(e)
Comments				
^a Observed value taken from Volkamer et al. (2001); ^b Observed values based on Elrod (2011); ^c Observed value taken from Nehr et al. (2011); ^d Observed values for glyoxal and methylglyoxal taken from Nishino et al. (2010); ^e Observed value taken from Nehr et al. (2012); ^f Observed values for biacetyl taken from Atkinson and Aschmann (1994) and Smith et al. (1999); ^g Observed value is total peroxide-bicyclic nitrate yield, based on Rickard et al. (2010) and Elrod (2011).				

S3 Phenol and cresols

As discussed in Sect. 3.2.1 of the main paper, the attack distributions predicted by the optimized parameters recreate some of the features inferred from reported experimental studies for phenol and cresols, but tend to underestimate the dominant *ortho*- directing effect inferred from reported product studies. It is generally recommended that attack distributions (and rate coefficients) based on the results of experimental studies are applied where evaluated information is available. Table S3 presents recommendations for phenol and the cresol isomers, informed by the product studies of Atkinson et al. (1992), Olariu et al. (2002) and Couer-Tourneur et al. (2006) each of which reports data for a series of phenolic compounds.

Table S3. Calculated and recommended branching ratios and rate coefficients (k) for OH attack for phenol and the cresol isomers at 298 K.

Attack site	Degeneracy	Branching ratios		
		Calculated	Recommended	Comment
1) phenol				
<i>ortho</i> - OH(1)	2	0.474	0.804	(a),(b)
<i>meta</i> - OH(2)	2	0.084	0.017	(c)
<i>para</i> - OH (3)	1	0.237	0.107	(a),(d)
<i>ipso</i> - OH (4)	1	0.042	0.009	(c)
abstraction -OH (5)	1	0.162	0.063	(a),(e)
$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)		16.0	28.0	
2) o-cresol				
<i>ortho</i> - OH, <i>meta</i> - CH ₃ (1)	1	0.160	0.734	(a),(b)
<i>ortho</i> - OH, <i>ipso</i> - CH ₃ (2)	1	0.156	-	(f)
<i>meta</i> - OH, <i>para</i> - CH ₃ (3)	1	0.147	-	(f)
<i>meta</i> - OH, <i>ortho</i> - CH ₃ (4)	1	0.147	-	(f)
<i>para</i> - OH, <i>meta</i> - CH ₃ (5)	1	0.160	0.198	(a),(d)
<i>ipso</i> - OH, <i>ortho</i> - CH ₃ (6)	1	0.144	-	(f)
abstraction -OH (7)	1	0.076	0.058	(a),(e)
abstraction -CH ₃ (8)	1	0.010	0.010	(g)
$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)		34.2	41.0	
3) m-cresol				
<i>ortho</i> - OH, <i>para</i> - CH ₃ (1)	1	0.288	0.097	(a),(b)
<i>ortho</i> - OH, <i>ortho</i> - CH ₃ (2)	1	0.288	0.686	(a),(b)
<i>meta</i> - OH, <i>meta</i> - CH ₃ (3)	1	0.059	-	(c)
<i>meta</i> - OH, <i>ipso</i> - CH ₃ (4)	1	0.015	-	(c)
<i>para</i> - OH, <i>ortho</i> - CH ₃ (5)	1	0.288	0.176	(a),(h)
<i>ipso</i> - OH, <i>meta</i> - CH ₃ (6)	1	0.015	-	(c)
abstraction -OH (7)	1	0.042	0.035	(a),(e)
abstraction -CH ₃ (8)	1	0.006	0.006	(g)
$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)		61.5	59.0	

Table S3 (continued). Calculated and recommended branching ratios and rate coefficients (*k*) for OH attack for phenol and the cresol isomers at 298 K.

Attack site	Degeneracy	Branching ratios		
		Calculated	Recommended	Comment
4) <i>p</i>-cresol				
<i>ortho</i> -OH, <i>meta</i> -CH ₃ (1)	2	0.320	0.641	(a),(b)
<i>meta</i> -OH, <i>ortho</i> -CH ₃ (2)	2	0.295	0.130	(c)
<i>para</i> -OH, <i>ipso</i> -CH ₃ (3)	1	0.156	0.068	(c)
<i>ipso</i> -OH, <i>para</i> -CH ₃ (4)	1	0.144	0.063	(c)
abstraction -OH (5)	1	0.076	0.088	(a),(e)
abstraction -CH ₃ (6)	1	0.010	0.010	(g)
$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)		34.2	49.0	
Comments				
^a Contribution (shown in red font) inferred from reported product yields (Atkinson et al., 1992; Olariu et al., 2002; Couer-Tourneur et al., 2006);				
^b Based on reported yield of corresponding catechol product;				
^c Contributions of these (minor) channels retain the calculated relative importance, but with their absolute contributions reduced to account for the residual not covered by (b), (d), (e) and (g);				
^d Based on reported yield of corresponding benzoquinone product, which is partially produced from the subsequent chemistry;				
^e Based on reported yield of corresponding 2-nitrophenol product;				
^f Assigned zero value, because full reaction is accounted for by product yields reported for other channels;				
^g Calculated contribution retained for abstraction from the CH ₃ group;				
^h Assigned branching ratio leads to underestimated formation of methyl-1,4-benzoquinone from subsequent chemistry, but is set at residual yield not covered by other routes.				

S4 Benzaldehydes

Table S4. Values of $k_{\text{abs(Ph-C(O)H)}}$ and $R_{\text{C(O)H}}(\Phi)$ at 298 K, optimized from the preferred data for benzaldehydes and methyl-substituted benzaldehydes, based on different assumptions. Method B is adopted (see Sect. 3.2.2 of the main paper).

	$10^{12} \times k_{\text{abs(Ph-C(O)H)}}$ cm ³ molecule ⁻¹ s ⁻¹	$R_{\text{C(O)H}}(o-)$	$R_{\text{C(O)H}}(p-)$	$R_{\text{C(O)H}}(m-)$	$R_{\text{C(O)H}}(ipso-)$	comment
A	10.8	0.25	0.25	0.78	0.78	(a)
B	12.1	0.096	0.096	0.096	0.096	(b)
C	12.6	0	0	0	0	(c)

Comments

^a Constant value of $k_{\text{abs(Ph-C(O)H)}}$, assumed to be unaffected by the presence of methyl substituents on the aromatic ring. Its value, and those of $R_{\text{C(O)H}}(\Phi)$, optimized using data for benzaldehyde and methyl-substituted benzaldehydes;

^b Adopted methodology (see Sect. 3.2.2 of main paper). Reference value of $k_{\text{abs(Ph-C(O)H)}}$ set to account for 96 % of the preferred rate coefficient for benzaldehyde, consistent with DFT study of Iuga et al. (2008). Strongly deactivating values of $R_{\text{C(O)H}}(\Phi)$ optimized so that OH addition accounts for the remaining 4 % of the reaction, with all factors assumed equivalent. Additional activating influence of methyl substituents on $k_{\text{abs(Ph-C(O)H)}}$ optimized using data for methyl-substituted benzaldehydes, leading to enhancement factors of 1.47, 1.30 and 1.30 for methyl groups positioned *ortho*-, *meta*- and *para*- to the -C(=O)H group, respectively;

^c OH addition to the aromatic ring assumed to be completely deactivated by the presence of a -C(O)H substituent. Additional activating influence of methyl substituents on $k_{\text{abs(Ph-C(O)H)}}$ optimized using data for methyl-substituted benzaldehydes, leading to enhancement factors of 1.51, 1.40 and 1.34 for methyl groups positioned *ortho*-, *meta*- and *para*- to the -C(=O)H group, respectively.

Table S5. Rate coefficients (in cm³ molecule⁻¹ s⁻¹) and -C(O)H abstraction contributions calculated with methods A, B and C (as described in Table S4) for benzaldehyde and related compounds at 298 K.

Compound	$10^{12} k_{\text{obs}}$	$10^{12} k_{\text{calc}}$			abstraction from -C(O)H		
		A	B	C	A	B	C
benzaldehyde	12.6	12.6	12.6	12.6	0.861	0.960	1.000
<i>o</i> -tolualdehyde	18.9	17.6	19.3	19.4	0.614	0.920	0.982
<i>m</i> -tolualdehyde	16.8	18.0	18.3	18.0	0.599	0.862	0.980
<i>p</i> -tolualdehyde	16.8	17.6	17.3	17.2	0.614	0.910	0.980
2,3-dimethylbenzaldehyde	25.5	23.4	27.0	27.8	0.461	0.856	0.960
2,4-dimethylbenzaldehyde	27.2	29.7	26.6	26.2	0.364	0.870	0.973
2,5-dimethylbenzaldehyde	27.6	23.4	27.0	27.8	0.461	0.856	0.960
2,6-dimethylbenzaldehyde	30.3	29.7	29.6	29.4	0.364	0.883	0.976
3,4-dimethylbenzaldehyde	24.4	23.4	24.3	24.8	0.461	0.840	0.955
3,5-dimethylbenzaldehyde	27.8	29.5	26.8	25.4	0.367	0.764	0.972
1,2-diformylbenzene	23.0	24.0	24.3	25.2	0.890	0.981	1.000
2-acetylbenzaldehyde ^a	17.0	13.4	12.3	12.7	0.795	0.953	0.990
1,2-diacetylbenzene ^a	< 1.2	2.7	0.38	0.26	- ^b	- ^b	- ^b

Comments

^a Optimized (or assigned) values of $R_{\text{C(O)H}}(\Phi)$ for -C(O)H groups are also assumed to apply to -C(O)CH₃ groups in these compounds; ^b Not applicable to 1,2-diacetylbenzene.

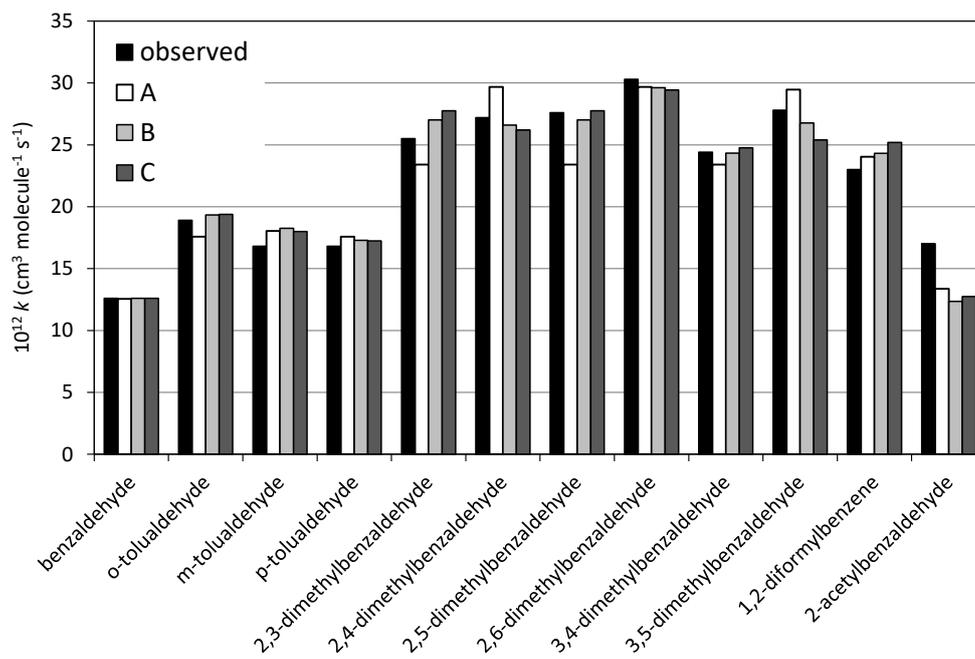
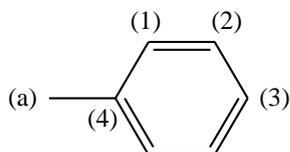


Figure S3. Comparison of observed (recommended) rate coefficients at 298 K for the reactions of OH with benzaldehyde and related compounds, with those estimated in the present work.

S5 OH + aromatic SAR application examples for 298 K

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

Example A: toluene



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

$$(1) k_{\text{arom}} \times F(o-) \times 2 = 0.2 \times 7.3 \times 2 = \mathbf{2.920}$$

$$(2) k_{\text{arom}} \times F(m-) \times 2 = 0.2 \times 1.4 \times 2 = \mathbf{0.560}$$

$$(2) k_{\text{arom}} \times F(p-) = 0.2 \times 7.3 = \mathbf{1.460}$$

$$(4) k_{\text{ipso}} = \mathbf{0.280}$$

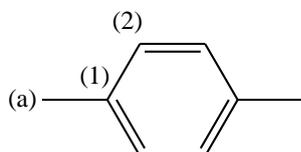
$$(a) k_{\text{prim}} \times F(-\text{Ph1}) = 0.13 \times 2.7 = \mathbf{0.351}$$

Total calculated rate coefficient: $5.57 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $5.60 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.524 (1): 0.101 (2): 0.262 (3): 0.050 (4): 0.063 (a)

Example B: *p*-xylene



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

$$(1) k_{\text{ipso}} \times F(p-) \times 2 = 0.28 \times 7.3 \times 2 = \mathbf{4.088}$$

$$(2) k_{\text{arom}} \times F(o-, m-) \times 4 = 0.2 \times 10.5 \times 4 = \mathbf{8.400}$$

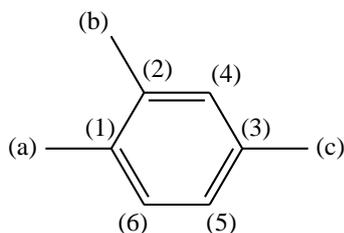
$$(a) k_{\text{prim}} \times F(-\text{Ph1}) \times \exp(140/T) \times 2 = 0.13 \times 2.7 \times 1.6 \times 2 = \mathbf{1.123}$$

Total calculated rate coefficient: $1.36 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $1.38 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.300 (1): 0.617 (2): 0.083 (a)

Example C: 1,2,4-trimethylbenzene



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

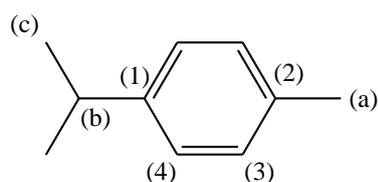
- (1) $k_{\text{ipso}} \times F(o-,p-) = 0.28 \times 34 = \mathbf{9.520}$
 (2) $k_{\text{ipso}} \times F(o-,m-) = 0.28 \times 10.5 = \mathbf{2.940}$
 (3) $k_{\text{ipso}} \times F(m-,p-) = 0.28 \times 10.5 = \mathbf{2.940}$
 (4) $k_{\text{arom}} \times F(o-,o-,m-) = 0.2 \times 28 = \mathbf{5.600}$
 (5) $k_{\text{arom}} \times F(o-,m-,p-) = 0.2 \times 28 = \mathbf{5.600}$
 (6) $k_{\text{arom}} \times F(o-,m-,m-) = 0.2 \times 11 = \mathbf{2.200}$
 (a) $k_{\text{prim}} \times F(-\text{Ph1}) \times [\exp(140/T)]^2 = 0.13 \times 2.7 \times 1.6^2 = \mathbf{0.899}$
 (b) $k_{\text{prim}} \times F(-\text{Ph1}) \times \exp(140/T) = 0.13 \times 2.7 \times 1.6 = \mathbf{0.562}$
 (c) $k_{\text{prim}} \times F(-\text{Ph1}) \times \exp(140/T) = 0.13 \times 2.7 \times 1.6 = \mathbf{0.562}$

Total calculated rate coefficient: $3.08 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $3.21 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.309 (1): 0.095 (2): 0.095 (3): 0.182 (4): 0.182 (5): 0.071 (6)
: 0.029 (a): 0.018 (b): 0.018(c)

Example D: *p*-cymene



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

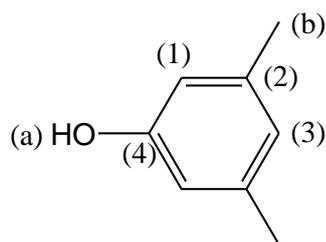
- (1) $k_{\text{ipso}} \times F(p-) = 0.28 \times 7.3 = \mathbf{2.044}$
 (2) $k_{\text{ipso}} \times F(p-) \times R_{i-pr}(p-) = 0.28 \times 7.3 \times 0.83 = \mathbf{1.697}$
 (3) $k_{\text{arom}} \times F(o-,m-) \times 2 = 0.2 \times 10.5 \times 2 = \mathbf{4.200}$
 (4) $k_{\text{arom}} \times F(o-,m-) \times R_{i-pr}(o-) \times 2 = 0.2 \times 10.5 \times 0.83 \times 2 = \mathbf{3.486}$
 (a) $k_{\text{prim}} \times F(-\text{Ph1}) \times \exp(140/T) = 0.13 \times 2.7 \times 1.6 = \mathbf{0.562}$
 (b) $k_{\text{tert}} \times F(-\text{Ph2}) \times \exp(140/T) \times F(-\text{CH}_3) \times F(-\text{CH}_3) = 1.49 \times 1.0 \times 1.6 \times 1.0 \times 1.0 = \mathbf{2.384}$
 (c) $k_{\text{prim}} \times F(-\text{CH}<) \times 2 = 0.13 \times 1.35 \times 2 = \mathbf{0.351}$

Total calculated rate coefficient: $1.47 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $1.47 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.139 (1): 0.115 (2): 0.285 (3): 0.237 (4): 0.038 (a): 0.162 (b)
: 0.024 (c)

Example E: 3,5-dimethylphenol



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

$$(1) k_{\text{arom}} \times F(o-,o-,p-) \times R_{\text{OH}}(o-) \times 2 = 0.2 \times 87 \times 2.6 \times 2 = \mathbf{90.480}$$

$$(2) k_{\text{ipso}} \times F(m-,m-) \times R_{\text{OH}}(m-) \times 2 = 0.28 \times 7.5 \times 2.4 \times 2 = \mathbf{10.080}$$

$$(3) k_{\text{arom}} \times F(o-,o-,p-) \times R_{\text{OH}}(p-) = 0.2 \times 87 \times 2.6 = \mathbf{45.240}$$

$$(4) k_{\text{ipso}} \times F(m-,m-) \times R_{\text{OH}}(\text{ipso-}) = 0.28 \times 7.5 \times 2.4 = \mathbf{5.040}$$

$$(a) k_{\text{abs(Ph-OH)}} = \mathbf{2.600}$$

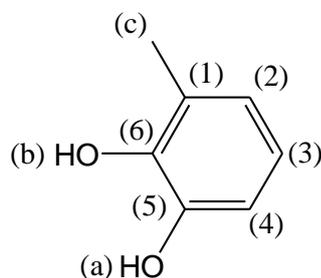
$$(b) k_{\text{prim}} \times F(-\text{Ph1}) \times 2 = 0.13 \times 2.7 \times 2 = \mathbf{0.702}$$

Total calculated rate coefficient: $1.54 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred (observed) rate coefficient: $1.13 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Calculated attack distribution: 0.587 (1): 0.065 (2): 0.293 (3): 0.033 (4): 0.017 (a): 0.005 (b)

Example F: 3-methyl-1,2-dihydroxybenzene



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

$$(1) k_{\text{ipso}} \times F(o-,m-) \times R_{\text{OH}}(o-) \times R_{\text{OH}}(m-) = 0.28 \times 10.5 \times 2.6 \times 2.4 = \mathbf{18.346}$$

$$(2) k_{\text{arom}} \times F(o-,m-,p-) \times R_{\text{OH}}(m-) \times R_{\text{OH}}(p-) = 0.2 \times 28 \times 2.4 \times 2.6 = \mathbf{34.944}$$

$$(3) k_{\text{arom}} \times F(m-,m-,p-) \times R_{\text{OH}}(m-) \times R_{\text{OH}}(p-) = 0.2 \times 11 \times 2.4 \times 2.6 = \mathbf{13.728}$$

$$(4) k_{\text{arom}} \times F(o-,m-,p-) \times R_{\text{OH}}(o-) \times R_{\text{OH}}(m-) = 0.2 \times 28 \times 2.6 \times 2.4 = \mathbf{34.944}$$

$$(5) k_{\text{ipso}} \times F(o-,m-) \times R_{\text{OH}}(\text{ipso-}) \times R_{\text{OH}}(o-) = 0.28 \times 10.5 \times 2.4 \times 2.6 = \mathbf{18.346}$$

$$(6) k_{\text{ipso}} \times F(o-,o-) \times R_{\text{OH}}(\text{ipso-}) \times R_{\text{OH}}(o-) = 0.28 \times 34 \times 2.4 \times 2.6 = \mathbf{59.405}$$

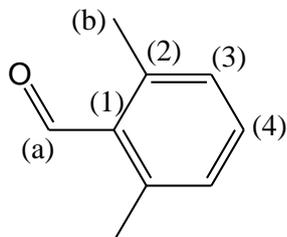
$$(a) k_{\text{abs(Ph-OH)}} = \mathbf{2.600}$$

$$(b) k_{\text{abs(Ph-OH)}} = \mathbf{2.600}$$

$$(c) k_{\text{prim}} \times F(-\text{Ph1}) = 0.13 \times 2.7 = \mathbf{0.351}$$

<u>Total calculated rate coefficient:</u>	$1.85 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
<u>Preferred (observed) rate coefficient:</u>	$2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
<u>Calculated attack distribution:</u>	0.099 (1): 0.189 (2): 0.074 (3): 0.189 (4): 0.099 (5): 0.321 (6): 0.014 (a): 0.014 (b): 0.002 (c)

Example G: 2,6-dimethylbenzaldehyde

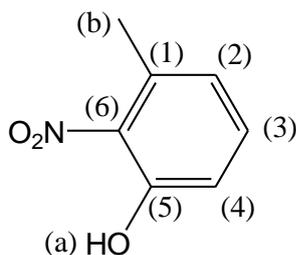


Partial rate coefficients (in units $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

- (1) $k_{\text{ipso}} \times F(o-,o-) \times R_{\text{C(O)H}}(\text{ipso-}) = 0.28 \times 34 \times 0.096 = \mathbf{0.914}$
- (2) $k_{\text{ipso}} \times F(o-,m) \times R_{\text{C(O)H}}(o-) \times 2 = 0.28 \times 10.5 \times 0.096 \times 2 = \mathbf{0.564}$
- (3) $k_{\text{arom}} \times F(o-,m-,p-) \times R_{\text{C(O)H}}(m-) \times 2 = 0.2 \times 28 \times 0.096 \times 2 = \mathbf{1.075}$
- (4) $k_{\text{arom}} \times F(m-,m-,p-) \times R_{\text{C(O)H}}(p-) = 0.2 \times 11 \times 0.096 = \mathbf{0.211}$
- (a) $k_{\text{abs(Ph-C(O)H)}} \times [\exp(115/T)]^2 = 12.1 \times 1.47^2 = \mathbf{26.147}$
- (b) $k_{\text{prim}} \times F(-\text{Ph}1) \times 2 = 0.13 \times 2.7 \times 2 = \mathbf{0.702}$

<u>Total calculated rate coefficient:</u>	$2.96 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
<u>Preferred (observed) rate coefficient:</u>	$3.03 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
<u>Calculated attack distribution:</u>	0.031 (1): 0.019 (2): 0.036 (3): 0.007 (4): 0.883 (a): 0.024 (b)

Example H: 3-methyl-2-nitrophenol



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

- (1) $k_{\text{ipso}} \times F(o-,m-) \times R_{\text{NO}_2}(o-) \times R_{\text{OH}}(m-) = 0.28 \times 10.5 \times 0.024 \times 2.4 = \mathbf{0.169}$
- (2) $k_{\text{arom}} \times F(o-,m-,p-) \times R_{\text{NO}_2}(m-) \times R_{\text{OH}}(p-) = 0.2 \times 28 \times 0.070 \times 2.6 = \mathbf{1.019}$
- (3) $k_{\text{arom}} \times F(m-,m-,p-) \times R_{\text{OH}}(m-) \times R_{\text{NO}_2}(p-) = 0.2 \times 11 \times 2.4 \times 0.024 = \mathbf{0.127}$
- (4) $k_{\text{arom}} \times F(o-,m-,p-) \times R_{\text{OH}}(o-) \times R_{\text{NO}_2}(m-) = 0.2 \times 28 \times 2.6 \times 0.070 = \mathbf{1.019}$
- (5) $k_{\text{ipso}} \times F(o-,m-) \times R_{\text{OH}}(\text{ipso-}) \times R_{\text{NO}_2}(o-) = 0.28 \times 10.5 \times 2.4 \times 0.024 = \mathbf{0.169}$

$$(6) k_{\text{ipso}} \times F(o-,o-) \times R_{\text{NO}_2}(\text{ipso-}) \times R_{\text{OH}}(o-) = 0.28 \times 34 \times 0.070 \times 2.6 = \mathbf{1.733}$$

$$(a) k_{\text{abs(-OH)}} = \mathbf{0.14}$$

$$(c) k_{\text{prim}} \times F(-\text{Ph1}) = 0.13 \times 2.7 = \mathbf{0.351}$$

$$\text{Total calculated rate coefficient: } 4.73 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

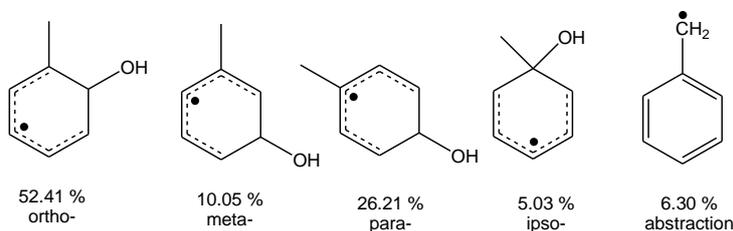
$$\text{Preferred (observed) rate coefficient: } 3.69 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\text{Calculated attack distribution: } 0.036 (1): 0.216 (2): 0.027 (3): 0.216 (4): 0.036 (5): 0.367 (6): \\ 0.030 (a): 0.074 (b)$$

S6 Toluene oxidation sequence example calculations

The reactions steps in the oxidation of toluene to first generation products are presented, with illustration of the rate coefficients and branching ratios for the steps involved.

1) Calculated initial attack distribution (see Sect. S5, Example A)



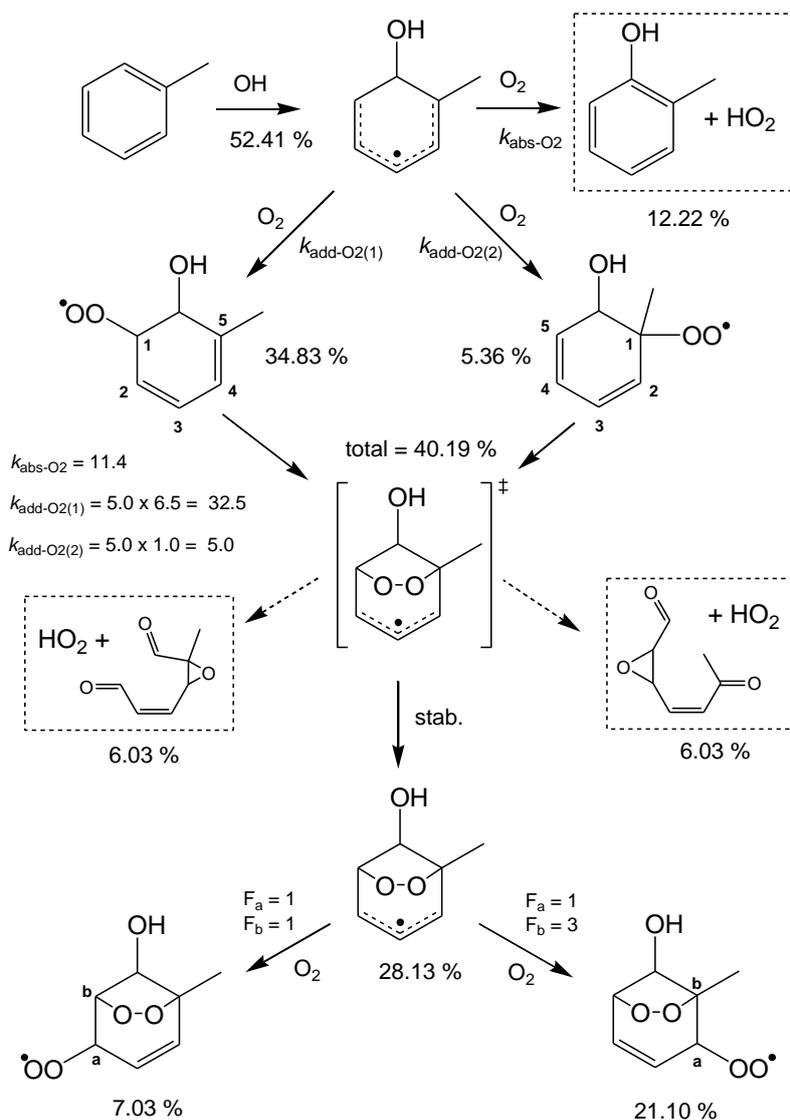
2) Reaction sequences following reaction with OH

a) ortho-OH addition ($k_{\text{abs-O}_2}$ and $k_{\text{add-O}_2}$ in units $10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

$$k_{\text{abs-O}_2} = 11.4$$

$$k_{\text{add-O}_2(1)} = k^{\circ}_{\text{add-O}_2} \times F_5(-\text{alkyl}) = 5.0 \times 6.5 = 32.5$$

$$k_{\text{add-O}_2(2)} = k^{\circ}_{\text{add-O}_2} \times F_1(-\text{alkyl}) = 5.0 \times 1.0 = 5.0$$

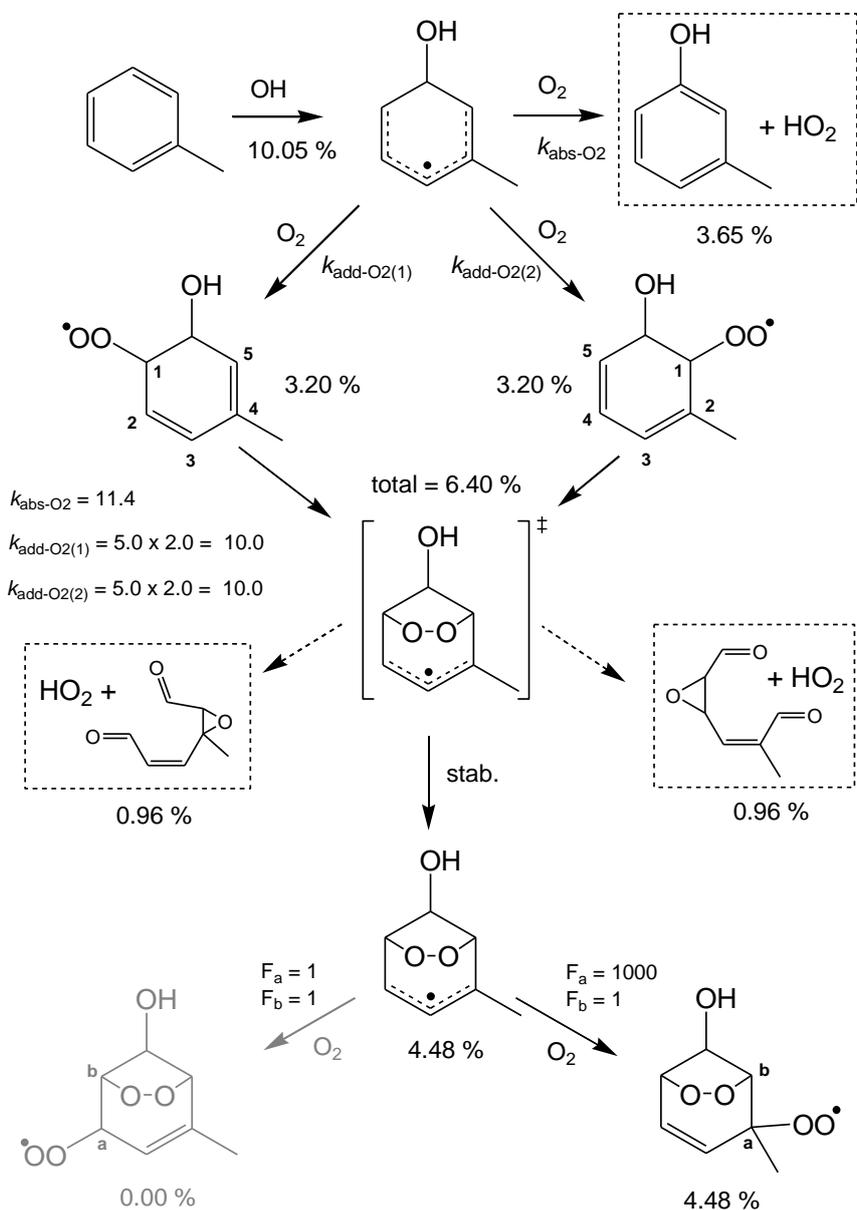


b) *meta*-OH addition ($k_{\text{abs-O}_2}$ and $k_{\text{add-O}_2}$ in units $10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

$$k_{\text{abs-O}_2} = 11.4$$

$$k_{\text{add-O}_2(1)} = k_{\text{add-O}_2}^\circ \times F_4(-\text{alkyl}) = 5.0 \times 2.0 = 10.0$$

$$k_{\text{add-O}_2(2)} = k_{\text{add-O}_2}^\circ \times F_2(-\text{alkyl}) = 5.0 \times 2.0 = 10.0$$

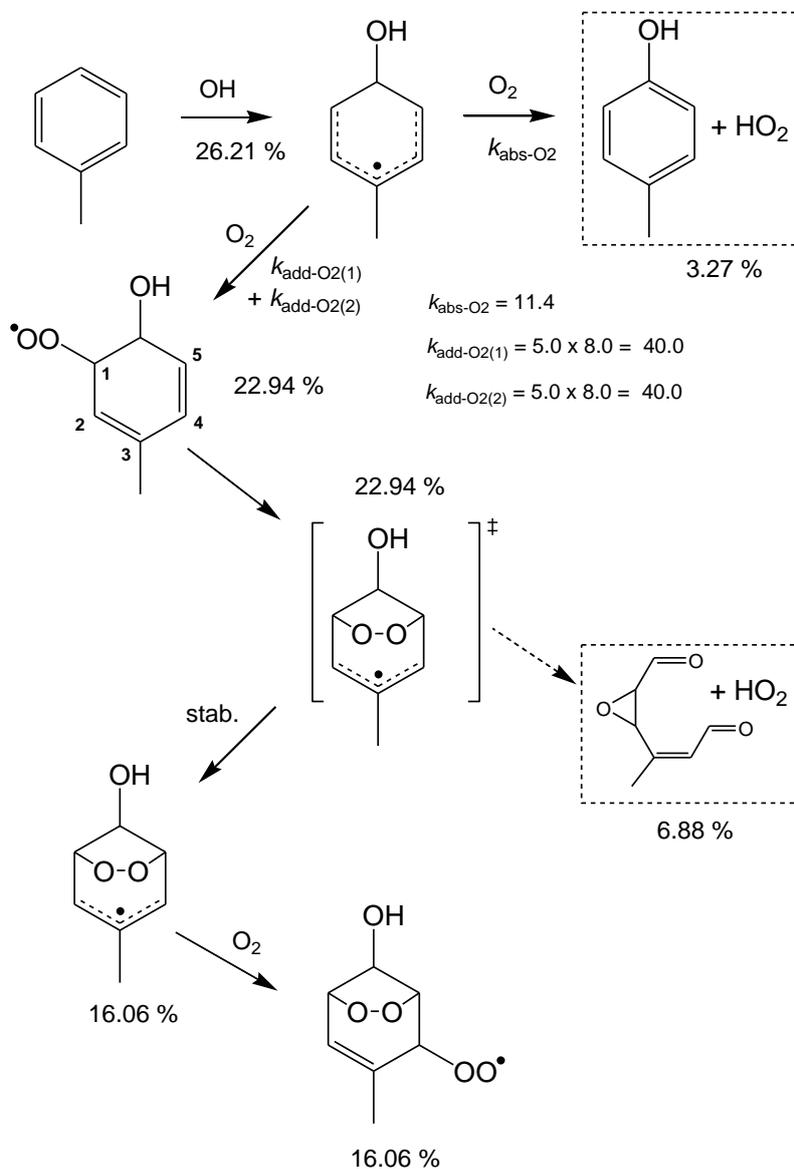


c) *para*-OH addition ($k_{\text{abs-O}_2}$ and $k_{\text{add-O}_2}$ in units $10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

$$k_{\text{abs-O}_2} = \mathbf{11.4}$$

$$k_{\text{add-O}_2(1)} = k_{\text{add-O}_2}^\circ \times F_3(-\text{alkyl}) = 5.0 \times 8.0 = \mathbf{40.0}$$

$$k_{\text{add-O}_2(2)} = k_{\text{add-O}_2}^\circ \times F_3(-\text{alkyl}) = 5.0 \times 8.0 = \mathbf{40.0}$$

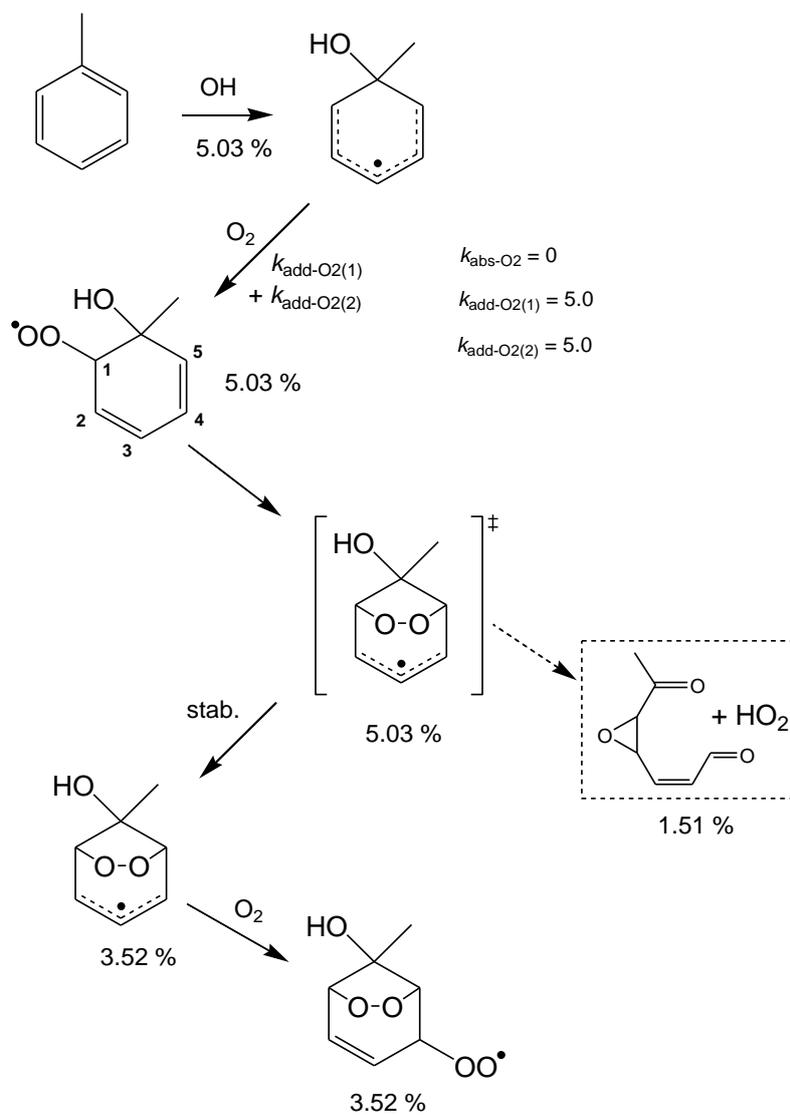


d) ipso- OH addition ($k_{\text{abs-O}_2}$ and $k_{\text{add-O}_2}$ in units $10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

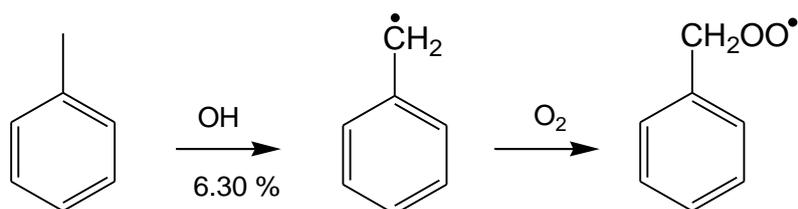
$k_{\text{abs-O}_2} = 0$ (no α -H)

$k_{\text{add-O}_2(1)} = k^{\circ}_{\text{add-O}_2} = 5.0$

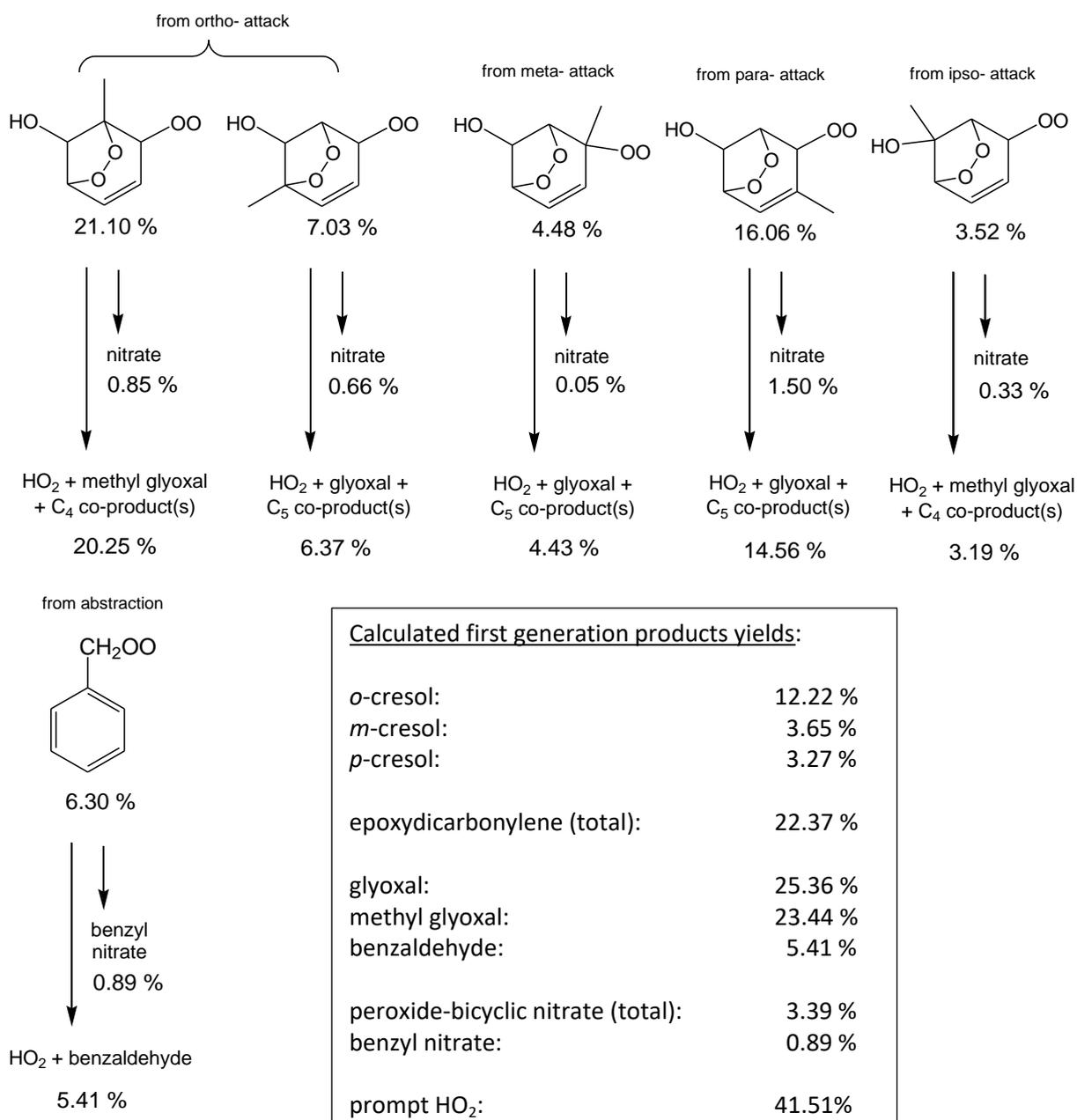
$k_{\text{add-O}_2(2)} = k^{\circ}_{\text{add-O}_2} = 5.0$



e) Abstraction



3) Product formation from exclusive reaction of peroxy radicals with NO



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