Kinetic and mechanistic study of the reaction of OH radicals with methylated benzenes: 1,4-dimethyl-, 1,3,5-trimethyl-, 1,2,4,5-, 1,2,3,5- and 1,2,3,4-tetramethyl-, pentamethyl-, and hexamethylbenzene

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S1 Experimental conditions

Table S1. Experimental conditions for 1,4-dimethylbenzene (14-DMB), 1,3,5-trimethylbenzene (135-TMB) and 1,2,4,5-tetramethylbenzene (1245-TeMB).

	14-DMB[a]				135-TMB[b]				1245-TeMB[c]			
Exp #	T / K	N[d]	min. conc.[e]	max. conc.[e]	T / K	N[d]	min. conc.[e]	max. conc.[e]	T / K	N[d]	min. conc.[e]	max. conc.[e]
1	304.3	12	10.0	63	299.1	21	0.85	17	300.2	10	4.9	20
2	305.0	27	8.5	66	300.2	7	0.88	11	300.5	11	4.7	20
3	305.7	26	10.0	71	300.3	9	0.88	12	302.8	11	4.9	19
4	314.4	26	9.8	67	300.8	29	0.87	13	306.3	12	4.7	19
5	324.6	26	6.7	70	303.1	29	0.89	13	306.8	14	4.8	19
6	333.9	11	10.0	52	303.4	23	0.82	13	310.0	14	4.7	19
7	343.0	27	8.7	68	305.0	29	0.90	13	314.3	14	4.5	20
8	352.3	27	8.4	74	305.5	10	0.86	13	314.8	13	4.7	19
9					307.7	21	0.86	13	319.9	7	4.6	19
10					308.2	29	0.87	13	323.7	14	4.8	19
11					315.1	21	0.84	13	324.7	14	4.6	19
12					324.1	21	0.82	13	333.9	13	5.1	20
13					333.1	29	0.81	13	334.1	14	4.6	20
14					341.8	29	0.93	13	342.7	12	4.8	20
15					348.1	27	1.7	13	343.2	12	4.9	19

Total pressure of He: [a] 230 mbar, [b] 200 mbar and [c] 246 mbar (except for experiments 4, 7, 10 and 11: 360 mbar). [d] Number of decay curves. [e] Concentrations in 10^{12}cm^{-3}.

Table S2. Experimental conditions for 1,2,3,4-tetramethylbenzene (1234-TeMB), 1,2,3,5-tetramethylbenzene (1235-TeMB) and pentamethylbenzene (PMB).

	1234-TeMB[a]				1235-TeMB[b]				PMB[a]			
Exp #	T / K	N[c]	min. conc.[d]	max. conc.[d]	T / K	N[c]	min. conc.[d]	max. conc.[d]	T / K	N[c]	min. conc.[d]	max. conc.[d]
1	298.8	17	0.50	3.1	297.6	51	0.88	17	299.8	12	1.00	7.7
2	303.8	17	0.50	3.1	302.8	35	0.92	17	300.9	31	0.43	7.5
3	305.6	27	0.49	3.1	304.2	30	0.88	17	303.4	15	0.80	8.1
4	313.2	16	0.80	3.1	305.2	31	0.87	17	305.4	15	0.91	7.6
5	324.6	14	1.10	3.1	308.8	36	0.91	17	311.4	15	1.00	8.0
6	334.0	13	0.80	3.2	312.5	39	0.86	17	313.3	15	0.77	7.6
7	343.3	18	0.47	3.1	316.8	38	0.86	17	314.0	15	0.79	7.1
8	352.3	12	1.50	3.1	320.9	28	0.80	17	323.2	15	0.82	8.0
9	361.8	18	0.49	3.1	326.1	33	0.80	17	324.4	15	0.95	7.6
10					330.2	39	0.80	17	328.3	15	0.99	7.1
11					335.4	36	0.80	17	332.2	15	0.98	7.1
12									337.9	15	1.00	7.5
13									342.1	15	0.89	6.9
14									357.6	15	0.94	7.5
15									362.3	15	0.96	7.6

Total pressure of He: [a] 230 mbar, [b] 200 mbar. [c] Number of decay curves. [d] Concentrations in 10^{12}cm^{-3}.

S2 Fit results

S2.1 Example plots

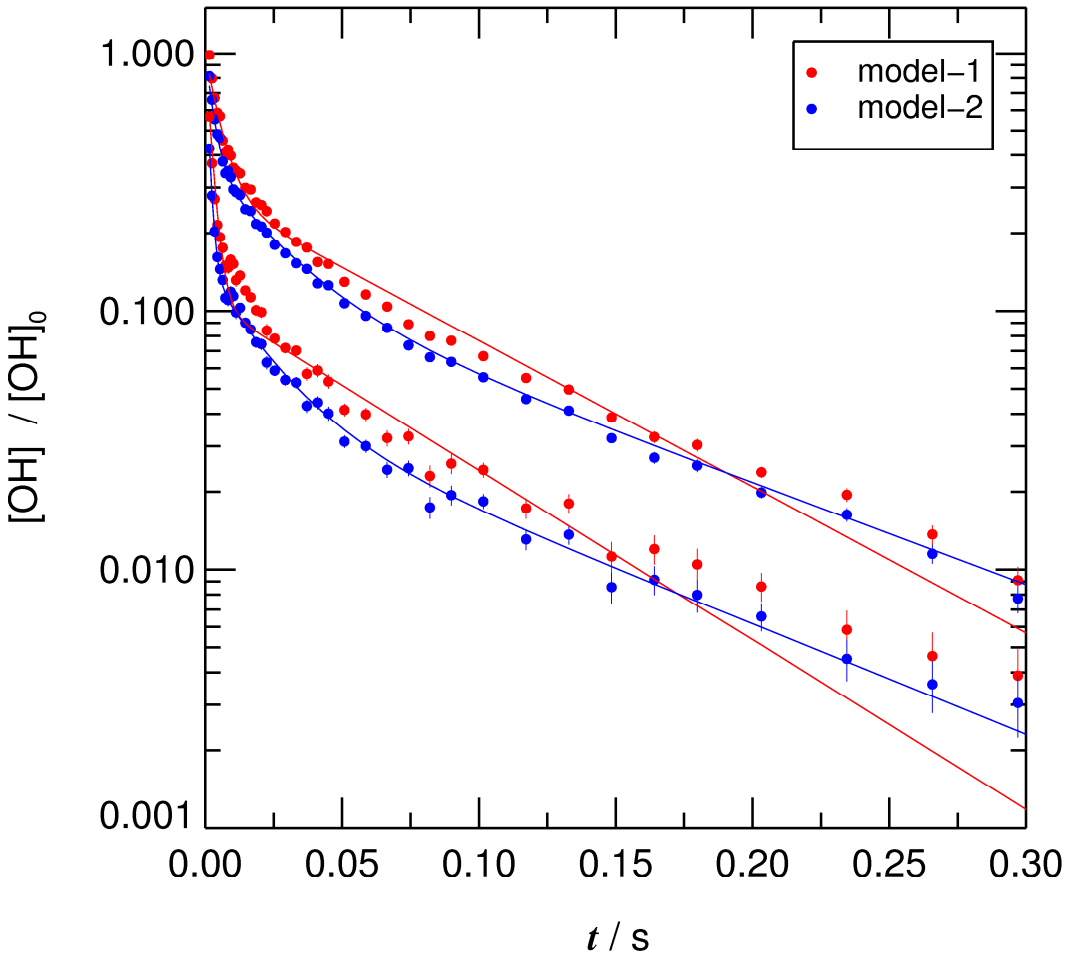

Fig S1. Examples of OH decay curves in a semi-logarithmic plot. Two from a total of eleven decay curves of the experiments with 14-DMB at 334 K are shown. At this temperature a maximum difference in fit qualities is apparent in Fig. 2 of the main paper. 14-DMB concentrations were 1.7×10^{13}cm^{-3} (top) and 5.0×10^{13}cm^{-3} (bottom). Full lines show the results of fits to all eleven decay curves simultaneously according to model-1 (red) and model-2 (blue). The data points were calculated from photon counts divided by interval widths and assigned to the middle of the intervals. Fitted backgrounds were subtracted and data then normalized to the fitted starting count rates. For that reason model-1 and model-2 data points are different even though they represent the same experimental decay curve. Only a small fraction of the total measurement time of 4 s is shown.

S2.2 Model-2

Table S3. Model-2 fit parameters for 14-DMB, 135-TMB and 1245-TeMB. Uncertainties are mean differences to upper and lower limit estimates.

Exp #	k_2 / s^{-1}	k_{OH} $=k_{11a}+k_{12a}+k_{1b}$ $/10^{-12}$ cm^3s^{-1}	k_{11a} k_{-11a} $/10^{-9}$ cm^3s^{-2}	$k_{-11a}+k_{31}$ / s^{-1}	k_{12a} k_{-12a} $/10^{-12}$ cm^3s^{-2}	$k_{-12a}+k_{32}$ / s^{-1}
14-DMB						
1	14 ± 9	13.3 ± 0.8	0.102 ± 0.016	15 ± 5	6 ± 13	3.1 ± 2.7
2	19 ± 7	12.5 ± 0.7	0.099 ± 0.017	17 ± 6	10 ± 15	3.8 ± 2.6
3	13 ± 10	12.9 ± 1.0	0.11 ± 0.02	21 ± 10	16 ± 21	4.9 ± 3.0
4	3.5 ± 3.9	12.9 ± 0.8	0.25 ± 0.03	35 ± 5	14 ± 8	6.1 ± 2.0
5	3.8 ± 1.7	12.4 ± 0.9	0.55 ± 0.08	71 ± 9	21 ± 8	11.0 ± 2.3
6	0.5 ± 1.0	12.7 ± 1.1	1.2 ± 0.2	145 ± 13	35 ± 8	19.6 ± 2.4
7	1.8 ± 1.6	11.6 ± 2.1	2.1 ± 0.7	259 ± 43	47 ± 18	32.6 ± 5.9
8	2.0 ± 2.0	11.4 ± 2.9	3.4 ± 1.2	430 ± 120	51 ± 35	48 ± 14
135-TMB						
1	22 ± 9	70.0 ± 8.0	0.31 ± 0.07	10.0 ± 4.4	30 ± 55	2.1 ± 2.1
2	20 ± 4	68.0 ± 4.0	0.32 ± 0.06	12.3 ± 3.7	56 ± 53	3.1 ± 1.5
3	26 ± 4	69.8 ± 4.2	0.31 ± 0.10	19 ± 11	140 ± 80	4.7 ± 1.5
4	8 ± 12	68.5 ± 6.2	0.32 ± 0.08	16.0 ± 8.1	86 ± 69	3.7 ± 1.6
5	25 ± 5	62.9 ± 3.8	0.41 ± 0.10	16.6 ± 7.2	89 ± 89	4.6 ± 2.2
6	22 ± 3	67.1 ± 4.0	0.41 ± 0.11	18 ± 11	130 ± 120	5.3 ± 2.2
7	16 ± 3	64.1 ± 3.8	0.49 ± 0.07	17.5 ± 4.7	85 ± 65	4.7 ± 1.7
8	18 ± 3	65.2 ± 3.9	0.58 ± 0.09	21.4 ± 6.4	120 ± 80	5.6 ± 1.6
9	14 ± 2	64.4 ± 3.9	0.67 ± 0.10	22.1 ± 7.1	110 ± 100	6.1 ± 2.3
10	17 ± 2	63.1 ± 3.8	0.69 ± 0.08	22.6 ± 6.1	110 ± 80	5.8 ± 1.9
11	13 ± 2	64.5 ± 5.8	1.6 ± 0.3	44.3 ± 9.6	160 ± 110	9.9 ± 2.8
12	7.4 ± 0.8	66.0 ± 7.9	4.3 ± 0.8	90 ± 12	135 ± 71	15.2 ± 3.4
13	5.2 ± 0.5	64.5 ± 9.7	9.7 ± 2.3	183 ± 22	92 ± 45	21.0 ± 4.4
14	4.6 ± 0.4	51.4 ± 9.3	14.2 ± 4.3	325 ± 45	51 ± 25	26.2 ± 5.5
15	4.8 ± 0.8	39.6 ±12.0	14.5 ± 7.3	430 ± 90	28 ± 18	26.4 ± 7.2
1245-TeMB						
1	−22 ± 1	57.8 ± 5.2	0.54 ± 0.07	34.8 ± 5.8	13 ± 24	3.2 ± 4.6
2	−4.4 ± 0.1	55.5 ± 5.0	0.48 ± 0.09	42 ± 12	40 ± 34	4.7 ± 3.2
3	12 ± 17	53.6 ± 4.8	0.61 ± 0.09	41 ± 10	30 ± 37	4.6 ± 4.1
4	32 ± 22	51.7 ± 4.7	0.83 ± 0.14	55 ± 10	46 ± 19	4.4 ± 1.7
5	11 ± 14	51.4 ± 4.6	0.86 ± 0.13	54.2 ± 8.1	46 ± 17	4.7 ± 1.4
6	29 ± 16	48.7 ± 4.4	1.07 ± 0.16	68.6 ± 9.4	64 ± 14	5.1 ± 0.9
7	23 ± 15	49.2 ± 4.4	1.46 ± 0.26	93 ± 13	89 ± 16	6.4 ± 1.0
8	16 ± 14	47.1 ± 4.2	1.45 ± 0.26	93 ± 14	107 ± 24	8.7 ± 1.3
9	25 ± 10	44.9 ± 4.0	2.21 ± 0.51	142 ± 21	170 ± 30	11.4 ± 1.0
10	23 ± 10	44.9 ± 5.4	2.87 ± 0.78	184 ± 33	220 ± 30	14.0 ± 1.3
11	8.7 ± 6.7	44.5 ± 4.7	2.94 ± 0.80	194 ± 32	240 ± 30	15.3 ± 1.1
12	25 ± 6	34.1 ± 6.2	3.3 ± 2.1	300 ± 100	460 ± 70	30.4 ± 2.3
13	17 ± 5	39.2 ± 5.9	3.7 ± 1.7	270 ± 70	400 ± 60	25.5 ± 1.5
14	10 ± 6	35.6 ± 14.1	4.4 ± 6.7	380 ± 310	790 ± 480	51 ± 18
15	18 ± 4	32.6 ± 10.5	3.4 ± 4.6	320± 230	690 ± 300	49 ± 8

S2.3 Model-3

Table S4. Model-3 fit parameters for 14-DMB, 135-TMB and 1245-TeMB. Parameters k_2 and k_{0H} are the same as for model-2. Uncertainties are mean differences to upper and lower limit estimates.

Exp #	$k_{11a}\,k_{-11a}$ $/10^{-9}$ cm^{3}s^{-2}	$k_{-11a}+k_{12}+k_{31}$ / s^{-1}	$k_{12}\,k_{21}$ / s^{-2}	$k_{21}+k_{32}$ / s^{-1}
14-DMB				
1	0.108 ± 0.015	14.7 ± 3.0	8 ± 18	3.8 ± 4.4
2	0.109 ± 0.018	16.2 ± 4.1	15 ± 31	5.0 ± 2.3
3	0.124 ± 0.025	18.9 ± 6.1	27 ± 71	6.9 ± 2.3
4	0.264 ± 0.032	33.5 ± 4.6	38 ± 28	7.5 ± 2.9
5	0.57 ± 0.09	68.9 ± 7.3	120 ± 56	13.1 ± 3.2
6	1.24 ± 0.21	141 ± 13	420 ± 130	23.0 ± 3.5
7	2.1 ± 0.7	254 ± 43	1100 ± 470	37.6 ± 6.8
8	3.5 ± 1.1	420 ± 120	2100 ± 1700	54 ± 17
135-TMB				
1	0.34 ± 0.06	9.3 ± 3.0	5 ± 12	2.8 ± 2.1
2	0.38 ± 0.06	11.0 ± 2.5	11 ± 15	4.4 ± 2.2
3	0.45 ± 0.10	14.9 ± 6.6	46 ± 98	9.3 ± 6.9
4	0.41 ± 0.08	13.5 ± 4.8	25 ± 50	6.3 ± 4.5
5	0.50 ± 0.08	14.5 ± 4.3	21 ± 42	6.7 ± 4.5
6	0.54 ± 0.12	15.3 ± 6.5	32 ± 87	8.4 ± 7.1
7	0.57 ± 0.08	15.7 ± 3.4	21 ± 25	6.5 ± 3.1
8	0.70 ± 0.11	18.8 ± 4.1	35 ± 39	8.2 ± 4.1
9	0.78 ± 0.13	19.9 ± 4.7	30 ± 46	8.3 ± 5.0
10	0.79 ± 0.11	20.4 ± 3.8	32 ± 36	8.0 ± 3.9
11	1.80 ± 0.32	41.3 ± 8.2	94 ± 90	12.9 ± 5.1
12	4.5 ± 0.8	88 ± 12	160 ± 100	17.5 ± 4.8
13	9.8 ± 2.4	182 ± 22	240 ± 120	22.5 ± 4.8
14	14.3 ± 4.3	324 ± 44	310 ± 150	27.3 ± 6.6
15	14.6± 7.3	428 ± 90	300 ± 190	27.2 ± 7.7
1245-TeMB				
1	0.55 ± 0.08	34.1 ± 5.3	21 ± 36	3.8 ± 2.6
2	0.52 ± 0.10	38.8 ± 11	94 ± 120	7.5 ± 5.8
3	0.64 ± 0.11	39.0 ± 7.7	55 ± 79	6.2 ± 6.1
4	0.87 ± 0.15	52.7 ± 8.8	127 ± 75	7.0 ± 2.8
5	0.91 ± 0.14	51.8 ± 7.8	116 ± 56	7.1 ± 2.4
6	1.14 ± 0.17	65.1 ± 8.9	210 ± 70	8.6 ± 1.8
7	1.55 ± 0.26	88 ± 12	400 ± 110	11.3 ± 1.7
8	1.56 ± 0.28	87 ± 13	450 ± 160	14.4 ± 2.6
9	2.38 ± 0.50	133 ± 20	1120 ± 280	20.6 ± 2.5
10	2.90 ± 0.78	172 ± 31	1870 ± 450	25.9 ± 3.1
11	3.09 ± 0.84	180 ± 33	2230 ± 540	28.8 ± 2.6
12	3.2 ± 0.9	270 ± 100	7900 ± 3400	63.3 ± 8.7
13	3.8 ± 2.2	248 ± 71	5300 ± 1700	49.2 ± 5.2
14	4.1 ± 1.8	330 ± 290	14000 ± 13000	101 ± 50
15	5.2 ± 7.3	280 ± 220	11000 ± 11000	95 ± 30

S2.4 Model-2/model-3 k_{OH} results for 1234-TeMB, 1235-TeMB and PMB

Because the number of possible adducts is greater than two for these compounds, model-2 and model-3 fits are regarded as approximations and only the presumably robust, common quantity k_{OH} is reported here.

Table S5. Rate constants of the reactions of OH with 1234-TeMB, 1235-TeMB and PMB. Uncertainties are mean differences to upper and lower limit estimates.

	1234-TeMB	1235-TeMB	PMB
Exp #	k_{OH} /10^{-12} cm^3s^{-1}	k_{OH} /10^{-12} cm^3s^{-1}	k_{OH} /10^{-12} cm^3s^{-1}
1	65.5 ± 2.6	62.6 ± 2.2	110.2 ± 6.6 [a]
2	61.9 ± 2.5	62.6 ± 3.7	109.7 ± 4.4 [a]
3	64.3 ± 3.6	60.4 ± 3.7	95.1 ± 3.8 [a]
4	61.0 ± 4.0	58.9 ± 3.5	91.7 ± 7.9
5	57.0 ± 7.6	62.6 ± 3.7	107.0 ± 7.6
6	45.7 ± 4.2	58.3 ± 3.5	97.0 ± 7.3
7	46.2 ± 5.2	60.1 ± 4.2	95.9 ± 6.3
8	43.1 ± 6.5	57.7 ± 4.6	96 ± 12
9	46 ± 10	53.3 ± 5.1	97 ± 11
10		61.9 ± 7.5	94 ± 14
11		53.3 ± 8.3	88 ± 12
12			96 ± 25
13			71.3 ± 3.6
14			59.1 ± 3.5
15			62.3 ± 4.2

[a] Model-1 result.

S2.5 Model-2 and model-3 equilibrium constants

Table S6. Equilibrium constants and estimated uncertainties for the direct formation of add_1 (K_{c1}) and add_2 (K_{c2}) and indirect formation of add_2 via isomerization (K_i).

Exp #	$K_{c1} = k_{11a}/k_{-11a}$ $/10^{-13}$ cm^3 model-2	$K_{c2} = k_{12a}/k_{-12a}$ $/10^{-13}$ cm^3 model-2	$K_{c1} = k_{11a}/k_{-11a}$ $/10^{-13}$ cm^3 model-3	$K_i = k_{12}/k_{21}$ model-3
14-DMB				
1	8.0 ± 4.7	19 ± 26	14.2 ± 6.0	0.75 ± 1.00
2	5.6 ± 3.9	16 ± 20	12.7 ± 4.0	0.74 ± 0.67
3	3.9 ± 3.4	12 ± 15	10.4 ± 3.2	0.67 ± 0.46
4	2.6 ± 0.6	5.9 ± 1.9	4.51 ± 0.54	0.80 ± 0.23
5	1.24 ± 0.19	2.2 ± 0.3	1.87 ± 0.17	0.78 ± 0.13
6	0.61 ± 0.07	1.05 ± 0.09	0.88 ± 0.08	0.84 ± 0.10
7	0.32 ± 0.05	0.48 ± 0.06	0.43 ± 0.05	0.81 ± 0.12
8	0.19 ± 0.05	0.24 ± 0.27	0.24 ± 0.05	0.75 ± 0.18
135-TMB				
1	84 ± 78	380 ± 530	180 ± 220	0.96 ± 1.29
2	46 ± 41	160 ± 190	128 ± 44	0.68 ± 0.52
3	13 ± 18	113 ± 39	99 ± 32	0.59 ± 0.28
4	22 ± 27	140 ± 120	103 ± 36	0.75 ± 0.40
5	26 ± 26	79 ± 54	74 ± 19	0.55 ± 0.31
6	19 ± 26	80 ± 32	76 ± 21	0.50 ± 0.23
7	26 ± 17	70 ± 23	65 ± 10	0.56 ± 0.19
8	19 ± 13	62 ± 15	54.3 ± 8.7	0.59 ± 0.19
9	20 ± 14	46 ± 12	45.8 ± 7.3	0.51 ± 0.16
10	20 ± 11	49 ± 11	44.9 ± 6.3	0.57 ± 0.15
11	10.0 ± 3.7	21.0 ± 3.2	18.9 ± 2.3	0.62 ± 0.14
12	5.8 ± 0.9	6.9 ± 1.0	7.81 ± 0.78	0.57 ± 0.09
13	3.0 ± 0.4	2.3 ± 0.4	3.46 ± 0.42	0.51 ± 0.07
14	1.38 ± 0.21	0.82 ± 0.12	1.49 ± 0.21	0.45 ± 0.06
15	0.81 ± 0.18	0.45 ± 0.08	0.85 ± 0.17	0.44 ± 0.08
1245-TeMB				
1	39 ± 35	260 ± 360	44 ± 54	1.9 ± 2.6
2	14 ± 19	80 ± 110	68 ± 89	1.9 ± 1.4
3	20 ± 18	67 ± 94	40 ± 40	1.7 ± 2.0
4	7.9 ± 3.8	130 ± 180	32 ± 18	3.0 ± 1.2
5	8.9 ± 3.5	100 ± 130	29 ± 11	2.7 ± 0.9
6	5.2 ± 1.4	98 ± 57	22.8 ± 6.3	3.2 ± 0.6
7	3.0 ± 0.6	58 ± 18	13.1 ± 2.7	3.4 ± 0.5
8	3.0 ± 0.8	28.2 ± 7.3	10.6 ± 2.1	2.3 ± 0.4
9	1.55 ± 0.28	21.3 ± 2.6	6.5 ± 1.1	2.8 ± 0.4
10	1.11 ± 0.19	16.5 ± 1.8	4.7 ± 0.8	2.9 ± 0.5
11	1.00 ± 0.17	14.9 ± 1.3	4.4 ± 0.7	2.8 ± 0.4
12	0.42 ± 0.12	5.9 ± 0.5	2.3 ± 0.8	2.0 ± 0.8
13	0.60 ± 0.12	7.5 ± 0.6	2.7 ± 0.6	2.2 ± 0.6
14	0.35 ± 0.42	3.3 ± 1.3	1.7 ± 1.6	1.4 ± 1.1
15	0.37 ± 0.42	3.2 ± 0.7	1.9 ± 1.1	1.2 ± 1.0

S3 Hexamethylbenzene

Experiments with hexamethylbenzene (HMB) made by von Buttlar et al.[1] were extensively re-evaluated in this work for direct comparison with the other investigated compounds using meanwhile developed software tools. Fit results are based on model-1. Von Buttlar et al.[1] typically recorded seven OH decay curves at different HMB concentrations in a range (4-10)×10^{11} cm^{-3} at a total pressure of 260 mbar of He. At temperatures below 330 K biexponential decay behaviour was not distinct enough to derive equilibrium constants. Some of the original experiments with suspected technical problems (298 K, 355 K) were rejected in the reanalysis.

Table S7. Model-1 fit parameters for HMB obtained in a re-evaluation of experiments by von Buttlar et al.[1]

T / K	k_2 / s^{-1}	$k_{OH} = k_{11a}+k_{1b}$ /10^{-12} cm^3s^{-1}	$k_{11a}\,k_{-11a}$ /10^{-9} cm^3s^{-2}	$k_{-11a}+k_{31}$ / s^{-1}	K_c [a] $= k_{11a}/k_{-11a}$ /10^{-13} cm^3
311.0	14.7 ± 2.5	139.7 ± 5.6	0.067 ± 0.040	9.7 ± 6.9	–
319.4	10.4 ± 2.3	136.0 ± 5.4	0.102 ± 0.027	8.3 ± 2.3	–
325.1	9.3 ± 2.5	129.8 ± 5.2	0.151 ± 0.040	11.2 ± 2.9	–
330.8	12.7 ± 1.9	126.6 ± 5.1	0.256 ± 0.031	11.1 ± 1.3	440 ± 650
334.9	9.5 ± 1.7	123.4 ± 4.9	0.347 ± 0.028	11.7 ± 0.9	380 ± 200
339.5	9.8 ± 1.7	119.7 ± 4.8	0.504 ± 0.040	13.0 ± 0.8	278 ± 80
345.0	8.4 ± 1.9	118.1 ± 4.7	0.792 ± 0.063	16.1 ± 1.0	144 ± 26
349.8	7.5 ± 1.1	117.3 ± 4.7	1.195 ± 0.072	20.0 ± 0.8	94.3 ± 6.7
360.3	8.0 ± 1.0	111.7 ± 4.5	2.56 ± 0.21	35.0 ± 1.4	37.1 ± 1.5
365.1	6.8 ± 0.7	104.4 ± 6.3	3.54 ± 0.35	46.9 ± 1.9	24.3 ± 1.0
370.3	7.2 ± 0.7	99.8 ± 10.0	5.25 ± 0.84	69.8 ± 5.6	14.1 ± 0.8

[a] Results for a fixed background loss rate constant k_{31}= 8.7 s^{-1}.

S4 Reactant vapour pressures

OH rate constants determined in this work rely on correct aromatic reactant concentrations. These concentrations were calculated from gas-flow rates and saturation vapour pressures of the compounds at the employed saturator temperatures (270-330 K, dependent on compound; accuracy: ±1 K). Reliable vapour pressure data from the literature are therefore critical for the determination of reactant concentrations.

In Table S8 available studies and their temperature range are summarised for the investigated aromatic compounds in the indicated phase (l = liquid, s = solid). The temperature of the saturator, the corresponding vapour pressures at saturator temperatures and coefficients for Antoine parameterisations that were applied are also listed. Vapour pressures for 14-DMB and 135-TMB have been reported in several publications with good agreement in a wide temperature range, including the saturator temperatures. For these compounds we used Antoine coefficients recommended by Stephenson et al.[2] In the case of 14-DMB the saturator temperature was accidentally set 2 K below the melting point at 286 K. No freezing was positively observed, so we are not sure about the phase during these experiments and Antoine coefficients for liquid 14-DMB were finally applied. In case the sample was solid, the vapour pressure would be lower by 5% (Tab. S8) and OH rate constants would increase accordingly by 5%.

No vapour pressure data were reported so far for 1245-TeMB(s), 1234-TeMB(l) and 1235-TeMB(l) at the saturator temperatures. For 1245-TeMB(s) we fitted Antoine coefficients to the low temperature data of Colomina et al.[3] and extrapolated to the saturator temperature. The resulting vapour pressure is in good agreement with a recommendation of Ruzicka Jr. et al.[4] that is based on an analysis of vapour pressures at higher temperatures and thermodynamic data. Vapour pressure measurements for the other two tetramethylbenzenes are only available in the form of parameterisations for temperatures much higher than the ones used in this study. An extrapolation of these data down to

the saturator temperatures is uncertain. Therefore, we preferred the recommendations of Ruzicka Jr. et al.[4] to fit Antoine coefficients.

For PMB, Colomina et al.[3] reported direct measurements covering the saturator temperature that were used to determine Antoine parameters. The measured data are also in good agreement with the recommendation by Ruzicka Jr. et al.[4]. For HMB, a large number of consistent vapour pressure data have been reported. In this case, the compilation published by Stephenson et al.[2] was used. In summary, we estimate maximum uncertainties of reactant concentrations of around 10% for 14-DMB, 135-TMB, PMB and HMB, and 20% for the three tetramethylbenzenes.

Table S8. Temperature range of literature studies on vapour pressures, saturator temperatures T_{sat} and corresponding vapour pressures P_{sat} of investigated compounds. Vapour pressures were calculated using parameterisations recommended in the various studies unless indicated otherwise. The Antoine equation: $\log_{10}[P_{sat}/\text{mbar}] = A - B / (T_{sat}/\text{K} + C)$ was applied in this work using the listed parameters.

Compound	T-range / K	A	B	C	T_{sat} / K	P_{sat} / mbar
14-DMB (l, s)	263–272[5]					– (s)[a]
	286–348[6]					5.01 (l)
	273–286[7]					4.70 (s)
	286–333[7]					5.00 (l)
	247–286[8]					4.69 (s)
	286–453[8]					4.98 (l)
	273–353[9]					4.38 (l)
	247–286[2]	16.501	6327.0	115.72		4.70 (s)
	286–453[2]	7.1478	1475.8	−55.24	284	4.97 (l)
135-TMB (l)	271–276[5]					– [a]
	273–373[9]					0.985
	255–268[10]					0.959[b]
	223–323[4]					0.940
	273–348[6]					0.942
	249–356[2]	7.6231	1810.7	−43.31	280	0.940
1245-TeMB (s)	271–275[5]					– [a]
	223–323[4]					0.812
	263–277[3]	10.704	3028	−32.8	313	0.790[a, b, c]
1234-TeMB (l)	333–478[11]					0.048[b]
	393–478[12]					– [a]
	223–323[4]					0.087
	223–323[4]	7.836	2083	−41.81	276	0.087[c]
1235-TeMB (l)	328–468[11]					0.573[b]
	223–323[4]					0.969
	223–323[4]	7.761	2007	−44.74	303	0.977[c]
PMB (s)	223–323[4]					0.091
	296–313[3]	2.973	333	−215.6	300	0.107[a, c]
HMB (s)	314–363[13]					– [a]
	303–343[14]					– [a]
	289–304[3]					– [a]
	223–323[4]					0.028
	303–343[2]	9.622	2966	−59.6	325	0.028

[a] No parameterisation given in the literature. [b] Extrapolated value, T_{sat} outside the studied range. [c] Antoine parameters from a fit to published data.

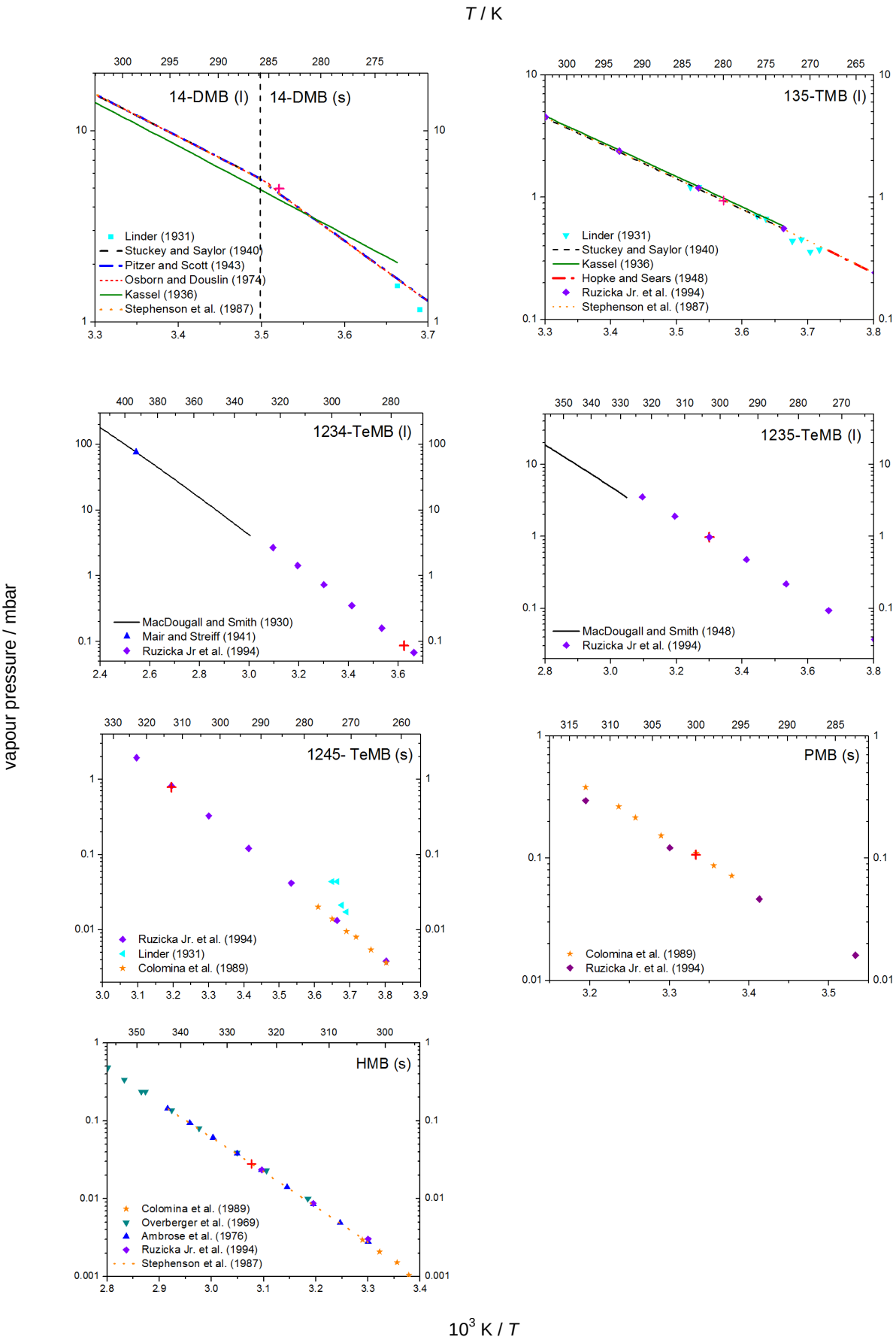

Fig S2. Vapour pressure data from the literature for the studied compounds. Crosses show the vapour pressures used for the determination of the aromatic concentrations in this study. For 14-DMB the vertical dashed line indicates the melting point.

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