



Supplement of

Intercomparison of the comparative reactivity method (CRM) and pump–probe technique for measuring total OH reactivity in an urban environment

R. F. Hansen et al.

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S1 Summary

This supplement consists of a map of the study area (Fig. S1), figures describing the characterizations made on the MD-CRM and UL-FAGE instruments (Figs. S2–S11), details about the synthetic VOC mixtures described in Sect. 3.1 of the main paper (Tables S1–S2), and measurements of ambient formaldehyde (HCHO) mixing ratios (Fig. S12).

Figures S3 and S5 detail the operating conditions of the MD-CRM instrument during the intercomparison. Figures S2, S6, and S7 show results of calibrations of various aspects of the MD-CRM instrument. Figures S4, S9, S10, and S11 demonstrate the performance of various aspects of the MD-CRM instrument during the intercomparison. Figure S8 presents the results of the measurements of standard mixtures described in Sect. 3.1 of the main text. Figure S12 shows a time series of HCHO measurements made during the intercomparison.

Table S3 presents the mechanism used for the simulation of OH decays from the pumpprobe instrument under various mixing ratios of NO, as described in Sect. 2.3.3 of the main text.



Figure S1. Map of the area surrounding the intercomparison site. The location of the site is indicated by a red star; major highways are indicated by black lines. (Map data © OpenStreetMap contributors (www.openstreetmap.org); used with permission under a Creative Commons BY-SA 2.0 license).



Figure S2. (a) PTR-ToFMS calibration curve for pyrrole with normalization to H_3O^+ signal only under wet (blue diamonds) and dry (red squares) conditions. (b) PTR-ToFMS calibration curve for pyrrole with normalization to the sum of the signal from H_3O^+ and 0.6 times the signal from H_3O^+ ·H₂O under wet (blue diamonds) and dry (red squares) conditions. All signals are normalized to 150000 cps of reagent ions.



Figure S3. Schematic illustrating the timing of the CRM measurements over a typical 12-hour period.



Figure S4. PTR-MS response factors (RF) (i.e., sensitivity) for pyrrole during the intercomparison exercise. RF factors measured under wet (blue) and dry (red) conditions. The gain on the PTR-ToFMS detector was increased after 9 October due to a sharp decrease of the PTR-ToFMS sensitivity but was held unchanged for the rest of the campaign.



Figure S5. Example of a C1 measurement, showing the evolution of the pyrrole signal. The points to the left of the box represent the C2 baseline.



Figure S6. Pyrrole mixing ratios (C2) as a function of the m37/m19 ($H_3O^+ \cdot H_2O/H_3O^+$) ratio. This figure shows tests conducted on 7 October 2012 (blue diamonds) and 12 October 2012 (red squares).



Figure S7. Difference in pyrrole signal (C3) due to $HO_2 + NO \rightarrow OH$ as a function of the NO mixing ratio in the CRM reactor. Tests were performed with (filled symbols) and without (open symbols) addition of ethane (equivalent to an OH reactivity of 24.4 s⁻¹).



Figure S8. Comparison of measured to calculated OH reactivity for the OVOC (panel a) and NMHC (panel b) mixtures for the pump-probe (blue circles) and CRM (red squares) instruments. The relative difference between the calculated OH reactivity and that measured by the CRM is shown as black squares.



Figure S9. Time series of the C1 concentration (black) and the pyrrole loss in the CRM reactor (blue) when the mercury lamp is turned on under C1 conditions (near-dry, see text).



Figure S10. Time series of standard additions for the CRM throughout the campaign. The line indicates the campaign average value of 24.6 s^{-1} . The relative standard deviation is 13%. The standard addition was equivalent to an OH reactivity of 24.4 s^{-1} .



Figure S11. Time series of ambient OH reactivity measurements from MD-CRM, including uncorrected measurements (blue diamonds), measurements corrected for differences in relative humidity between C2 and C3 (green diamonds), measurements corrected for differences in relative humidity and NO_x artifacts (orange diamonds), and measurements with all corrections applied (red squares).



Figure S12. Time series of ambient formaldehyde mixing ratios from 17–24 October 2012.

Table S1. Composition of the NMHC mixture, with selected absorption cross-sections and bimolecular rate constants for reaction with OH.

Compound	Mixing ratio in	Mixing ratios	Absorption cross-sections (×10 ⁻²⁰ cm ⁻²)			k _{OH} at 298K (×10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹)	
	cylinder	for tests	(from MPI Spectral Atlas				
	(ppmv)	(ppbv) ^a	(Keller-Rudek et al., 2013))			T T 1	D d
			185 nm	254 nm	266 nm	Value	Ref
Ethane	5.70	1.2–6.6	C	_	-	0.240	Atk06
Ethylene	5.85	1.2-6.8	30.5	_	-	7.90	Atk06
Propane	6.26	1.3–7.2	_	_	-	1.10	Atk06
Propene	5.99	1.2-6.9	1369	-	-	29.0	Atk06
Isobutane	6.45	1.3–7.5	_	-	-	2.12	Atk03
Acetylene	5.72	1.2–6.6	59.2	-	-	0.780	Atk06
<i>n</i> -Butane	6.98	1.4-8.1	_	_	_	2.36	Atk06
trans-2-butene	6.51	1.3-7.5	3140	_	-	64.0	IUPAC
1-butene	6.51	1.3-7.5	2030	_	-	31.0	IUPAC
cis-2-butene	7.00	1.4-8.1	2420	_	-	56.0	IUPAC
Isopentane	4.47	0.9-5.2	—	_	-	3.60	Atk03
n-Pentane	4.84	1.0-5.6	_	_	_	3.80	Atk03
1,3-butadiene	6.70	1.4–7.7	1911	_	_	66.6	AtA03
trans-2-pentene	4.57	0.9-5.3	4210	_	_	67.0	AtA03
1-pentene	4.84	1.0-5.6	3130	_	_	31.4	AtA03
cis-2-pentene	4.64	0.9-5.4	4210	_	_	65.0	AtA03
Isoprene	5.35	1.1-6.2	1284	5.28	0.191	100	Atk06
1-hexene	5.08	1.0-5.9	2320	_	_	37.0	AtA03
<i>n</i> -Hexane	4.47	0.9-5.2	_	_	_	5.20	Atk03
Benzene	5.23	1.1-6.0	3150	69.1	2.31	1.22	AtA03
Isooctane	5.51	1.1-6.4	_	_	_	3.34	Atk03
Heptane	5.93	1.2-6.9	_	_	_	6.76	Atk03
Toluene	5.23	1.1-6.0	16520	48.1	28.5	5.63	Atk03
<i>n</i> -Octane	5.19	1.1-6.0	_	_	_	8.11	Atk03
Ethylbenzene	5.00	1.0-5.8	_	46.1	45.3	7.00	AtA03
<i>m</i> , <i>p</i> -Xylene	5.14	1.0-5.9	19100 ^d	54.3 ^d	42.4 ^d	18.7 ^e	AtA03
o-Xylene	5.25	1.1-6.1	16800	62.3	53.4	13.6	AtA03
<i>n</i> -Nonane	0.97	0.2-1.1	_	_	_	9.7	Atk03
1,3,5-	0.97	0.2-1.1	6960	41.5	57.5	56.7	AtA03
trimethylbenzene							
1,2,4-	0.95	0.2-1.1	13900	52.5	135	32.5	AtA03
trimethylbenzene							
<i>n</i> -Decane	0.95	0.2-1.1	_	_	_	11.0	Atk03
1,2,3-	0.97	0.1-1.1	_	_	_	32.7	AtA03

trimethylbenzene

^aRange for 7 tests performed with this mixture; ^bAbbreviations corresponding to the following references: Atk06, (Atkinson et al., 2006); Atk03, (Atkinson, 2003); IUPAC, Database from IUPAC Kinetics Website (http://iupac.pole-ether.fr/); AtA03, (Atkinson and Arey, 2003); ^cNot reported; ^dValues for *m*-xylene; ^eAverage of rate constants for *m*- and *p*-xylene

Table S2. Composition of OVOC mixture, with selected absorption cross-sections and bimolecular rate constants for reaction with OH.

Compound	Mixing ratio in	Mixing ratios for	Absorption c $(\times 10^{-20} \text{ cm}^{-2})$	cross-sections	k(k _{OH} at 298K (×10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹)	
	cylinder	tosts	(^10 Cll) (from MPI S	nactral Atlas	(*	(^10 cm molecule s)	
	(nnmy)	(nnhy) ^a	(I OIII 1011 I Speculai Auas (Kollor-Rudok at al. 2013))				
	(ppmv)	(ppu)	185 nm	254 nm	, 266 nm	Value	Ref ^b
Furan	2 96	1 91-7 25	1080	_c	_	40.5	Atk85
2-methylfuran	2.98	1 93-7 30	836	58.0	28.3	61.9	Bie92
Toluene	2.98	1 93-7 30	16520	48.1	28.5	5 63	AtA03
Acetaldehvde	3.04	1.96-7.45	_	1.52	3.06	15.0	Atk06
ETBE ^d	2.93	1.89-7.18	_	_	_	8.70	AtA03
MTBE ^e	3.31	2.14-8.11	_	_	_	3.13	Bon92
TAME ^f	3.34	2.16-8.18	_	_	_	6.20	Tet96
Methacrolein	2.96	1.91-7.25	_	0.178	0.305	29.0	Atk06
Acetonitrile	2.86	1.85-7.01	0.0853	2.71	1.29	0.0220	Atk06
Butanal	3.00	1.94-7.35	1510	1.47	3.13	24.0	Atk06
Acetone	2.95	1.91-7.23	296	3.01	4.49	0.180	Atk06
Pentanal	3.43	2.22-8.40	_	1.47	3.06	28.0	Alb02
MVK ^g	2.98	1.93-7.30	_	0.241	0.499	20.0	Atk06
Ethyl acetate	3.00	1.94-7.35	42.1	_	-	1.82	Atk06
2-butanone	3.00	1.94-7.35	131	3.09	4.96	1.20	Atk06
Ethanol	3.15	2.04-7.72	118	_	_	3.20	Atk06
Hexanal	3.36	2.17-8.23	_	1.14	2.46	30.0	AtA03
Isopropanol	3.08	1.99–7.55	204	_	_	5.10	Atk06
2-pentanone	3.39	2.19-8.30	_	2.92	4.93	4.40	AtA03
Heptanal	3.39	2.19-8.30	_	_	-	30.0	AtA03
MIBK ^h	3.39	2.19-8.30	_	_	-	12.5	LeC98
Isobutanol	3.15	2.04-7.72	_	_	-	9.20	Mel04
<i>tert</i> -Butanol	3.39	2.19-8.30	_	_	-	1.08	Tet96
Butyl acetate	3.00	1.94–7.35	_	_	-	5.20	Vei96
2-hexanone	3.39	2.19-8.30	_	2.51	4.19	i	AtA03
<i>n</i> -Butanol	3.09	2.00-7.57	_	_	-	8.50	Atk06
Benzaldehyde	2.96	1.91-7.25	_	305 ^j	214	12.0	AtA03
2-heptanone	3.39	2.19-8.30	_	_	-	11.0	AtA03
3-methyl-2-	3.39	2.19-8.30	_	_		150	Ima04
hutan 1 al							

buten-1-ol

^aRange for 3 tests performed with this mixture; ^bAbbreviations corresponding to the following references: Alb02, (Albaladejo et al., 2002); Atk85, (Atkinson, 1985); AtA03, (Atkinson and Arey, 2003); Atk06, (Atkinson et al., 2006); Bie92, (Bierbach et al., 1992); Bon92, (Bonard et al., 1992); Ima04, (Imamura et al, 2004); Lec98, (Le Calve et al., 1998); Mel04, (Mellouki et al., 2004); Tet96, (Teton et al., 1996); Vei96, (Veillerot et al., 1996); ^cNot reported; ^dEthyl *tert*-butyl ether; ^eMethyl *tert*-butyl ether; ^f*tert*-amylmethyl ether; ^gMethyl vinyl ketone; ^hMethyl isobutyl ketone; ⁱValue of k_{OH} for 2-heptanone used; ^jAbsorption cross-section at 255 nm

n°	Reaction	k (cm ³ molecule ⁻¹ s ⁻¹)	Reference
1	$OH + CO \rightarrow HO_2 + CO_2$	2.23×10 ⁻¹³	(Atkinson et al., 2004) ^b
2	$OH + NO \rightarrow HONO$	9.6×10 ⁻¹²	(Atkinson et al., 2004) ^b
3	$OH + NO_2 \rightarrow HNO_3$	1.14×10 ⁻¹¹	(Atkinson et al., 2004) ^b
4	$OH \rightarrow wall loss$	5.6 s ^{-1(a)}	Measured
5	$OH + VOC \rightarrow RO_2 + H_2O$	1×10 ⁻¹²	Estimated (VOC adjusted)
6	$OH + CH_4 \rightarrow CH_3O_2 + H_2O$	5.78×10 ⁻¹⁵	(Atkinson et al., 2004) ^b
7a	$\rm HO_2 + \rm NO \rightarrow \rm OH + \rm NO_2$	8.62×10 ⁻¹²	(Atkinson et al., 2004) ^b
7b	$\mathrm{HO}_2 + \mathrm{NO} + \mathrm{M} \rightarrow \mathrm{HNO}_3 + \mathrm{M}$	4.56 ×10 ⁻¹⁴	(Atkinson et al., 2004) ^b
8	$HO_2 + NO_2 \rightarrow HO_2NO_2$	7.45×10 ⁻¹³	(Atkinson et al., 2004) ^b
9	$HO_2NO_2 \rightarrow HO_2 + NO_2$	0.03	(Atkinson et al., 2004) ^b
10	$\mathrm{HO}_2 + \mathrm{HO}_2 \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2$	2.93×10 ⁻¹²	(Atkinson et al., 2004) ^b
11	$\mathrm{HO}_2 + \mathrm{CH}_3\mathrm{O}_2 \rightarrow \mathrm{CH}_3\mathrm{OOH} + \mathrm{O}_2$	5.44×10 ⁻¹²	(Atkinson et al., 2004) ^b
12	$CH_3O_2 + NO \rightarrow HO_2 + HCHO$	7.86×10 ⁻¹²	(Atkinson et al., 2004) ^b
13	$CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$	5.95×10 ⁻¹²	(Atkinson et al., 2004) ^b
14	$CH_3O_2 + OH \rightarrow products$	2.8×10 ⁻¹⁰	(Bossolasco et al., 2014)
15	$RO_2 + NO \rightarrow HO_2 + CARB$	1×10 ⁻¹¹	Estimated ^c
16	$RO_2 + NO_2 \rightarrow products$	7.0×10 ⁻¹²	Estimated ^c
17	$RO_2 + OH \rightarrow products$	1.2×10^{-10}	(Faragó et al., 2014)
18	$HO_2 \rightarrow wall \ loss$	0.5 *	Estimated
19	$CH_3O_2 \rightarrow wall \ loss$	0.5 *	Estimated
20	$RO_2 \rightarrow wall \ loss$	0.5 *	Estimated
21	$NO + O_3 \rightarrow NO_2 + O_2$	1.74×10 ⁻¹⁴	(Atkinson et al., 2004) ^b

Table S3. Chemical mechanism used for the simulations of decays from the pump-probe instrument.

^arate constant has units of s⁻¹ ^b293K, 700 Torr

^cEstimated from average of rate constants for several larger peroxy radicals as given in (Atkinson et al., 2004)

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