atmosphere

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Supporting Information

Table S1. Studies below room temperature for the reaction of OH radicals with hydrocarbons.

Compounds	Technique*	Temperature Range (K)	Reference
n-butane	RR (relative to ethane, k=1.49×10^{-17} $T^2e^{-499/T}$)	235–361	DeMore and Bayes [1]
	PLP-LIF	231–378	Talukdar et al. [2]
n-pentane	RR (relative to *n*-butane, k=1.81×10^{-17} $T^2e^{114/T}$)	233–364	DeMore and Bayes [1]
	RR (relative to 2-methylpropane, k=1.17×10^{-17} $T^2e^{213/T}$)	243–325	Harris and Kerr [3]
	PLP–LIF	224–372	Talukdar et al. [2]
n–hexane	RR/DF/MS	240–340	Crawford et al. [4]
n–heptane	RR/DF/MS	240–340	Crawford et al. [4]
	RR (relative to several hydrocarbons)	241/406	Wilson et al. [5]
n–octane	RR/DF/MS	240–340	Li et al. [6]
n–nonane	RR/DF/MS	240–340	Li et al. [6]
cyclooctane	HPFS	237–379	Sprengnether et al. [7]
	RR/DF/MS	240–340	Singh et al. [8]
2,2–dimethylbutane	RR (relative to *n*–pentane, k=2.52×10^{-17} $T^2e^{158/T}$)	245–328	Harris and Kerr [3]
Benzene	FPRF	250–298	Tully et al. [9]
	FPRF	239–352	Witte et al. [10]
	RR (relative to toluene, k=0.79×10^{-12} $e^{614/T}$)	274–363	Semadeni et al. [11]
Toluene	FPRF	213–352	Tully et al. [9]
o–xylene	RR/DF/MS	240–340	Mehta et al. [12]
p–xylene	RR/DF/MS	240–340	Mehta et al. [12]
	FPRF	300–350	Alarcón et al. [13]

*RR: relative rate

PLP–LIF: pulsed laser photolysis–laser induced fluorescence

DF: discharge flow

MS: mass spectrometry

HPFS: high pressure flow system

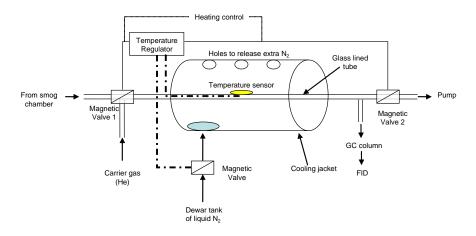FPRF: flash photolysis resonance fluorescence

Figure S1. Schematic flowchart of the sample enrichment system connected with gas chromatographic analysis of the gas phase in the smog chamber.

S1. Gas containers to introduce hydrocarbons into chamber

Two gas containers (1.3 L each) were used to introduce the hydrocarbons into the smog chamber. Gas container 1 was filled with the 13 compounds *n*–butane, *n*–pentane, *n*–hexane, *n*–heptane, *n*–octane, *n*–nonane, cyclooctane, 2,2–dimethylbutane, 2,2–dimethylpentane, 2,2–dimethylhexane, 2,2,4–trimethylpentane, benzene and *n*–perfluorohexane, and gas container 2 was filled with the other 5 hydrocarbons (2,2,3,3–tetramethylbutane and the aromatics toluene, ethylbenzene, p–xylene and o–xylene). The stock concentration of each of the hydrocarbons was around 1300 ppm in the gas container. By taking 50 ml gas samples from each container by a gas–tight syring, and initial concentrations of about 20 ppb were obtained in the smog chamber.
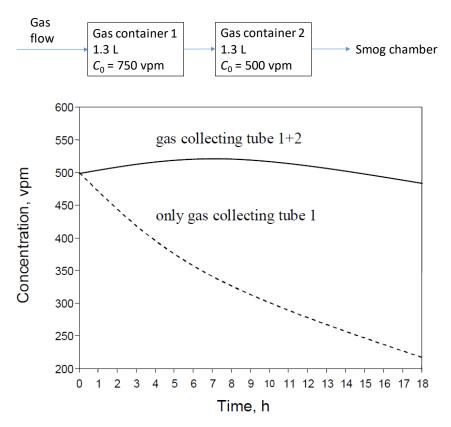

Figure S2. Dosage of methyl nitrite into the smog chamber, using a twin of gas containers. This method warrants a fairly constant production of OH [14].

S2. Hydrocarbons used in the experiments

n–Butane (liquid gas bottle, AIR LIQUIDE Deutschland GmbH), *n*–pentane (Grüssing GmbH), *n*–hexane (Merck kGaA, UniSolv), *n*–heptane (Fluka AG, UV Spectroscopy grade), *n*–octane (Fluka AG), *n*–nonane (Riedel–de Haen AG), cyclooctane (Sigma–Aldrich), 2,2–dimethylbutane (Janssen Chimica), 2,2–dimethylpentane (Janssen Chimica), 2,2–dimethylhexane (Sigma–Aldrich), 2,2,4–trimethylpentane (Janssen Chimica), 2,2,3,3–tetramethylbutane (Sigma–Aldrich), benzene (Riedel–de Haen AG), toluene (Carl Roth GmbH&Co KG), ethylbenzene (Riedel–de Haen AG), *p*–xylene (Fluka AG), *o*–xylene (Fluka AG), *n*–perfluorohexane (Sigma–Aldrich)

S3. Illustration of the Twin of Gas Containers to Inject Methyl Nitrite into Chamber

A twin of gas containers (1.3 L of each) were connected one by another and known volumes of methyl nitrite were injected into the gas containers by a syringe respectively. The gaseous methyl nitrite was slowly flushed by air into the chamber. With the aid of the twin of gas collecting tubes, an approximately constant concentration of OH was maintained during the experiment [1].
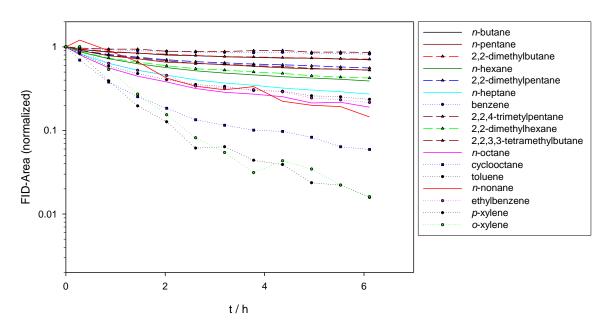

Figure S3. Decrease of the hydrocarbon concentrations (normalized by *n*–perfluorohexane) by the reaction with OH during a smog chamber run at 248 K.
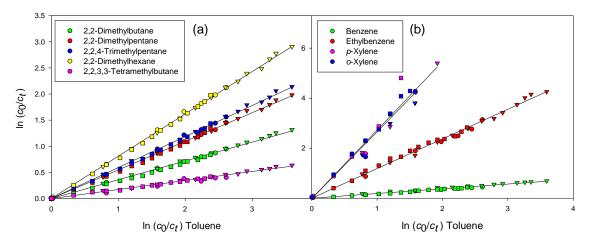

Figure S4. Plots of ln (c_0/c_t) of hydrocarbons versus toluene (reference substance) from data points of three experimental runs at 288 K, respectively (▽, ○ and □ distinguish data points from different experimental runs). (**a**) branched–chain alkanes; (**b**) aromatic hydrocarbons.
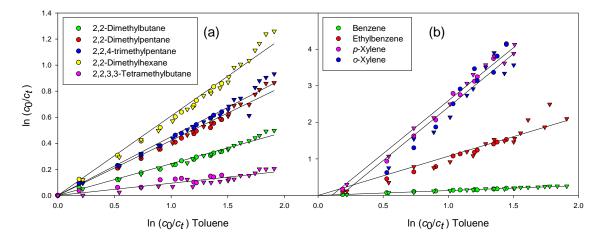
Figure S5. Plots of ln (c_0/c_t) of hydrocarbons versus toluene (reference substance) from data points of two experimental runs at 248 K, respectively ($\triangledown$ and $\circ$ distinguish data points from different experimental runs). (**a**) branched–chain alkanes; (**b**) aromatic hydrocarbons.

Table S2. Rate constants for the reaction of OH radicals with hydrocarbons at 248K.

Compound	Rate constant, $(k_{OH} \pm 2\sigma)$ / 10^{-12} cm^3 s^{-1}		
	Toluene as Reference [a]	Pentane as Reference [b]	Average
n–Butane	1.74 ± 0.03	1.59 ± 0.02	1.66 ± 0.04
n–Pentane	3.19 ± 0.03	2.93^b	3.06 ± 0.03
n–Hexane	4.79 ± 0.08	4.56 ± 0.09	4.68 ± 0.12
n–Heptane	6.51 ± 0.10	6.32 ± 0.14	6.42 ± 0.17
n–Octane	8.16 ± 0.16	7.97 ± 0.20	8.07 ± 0.26
n–Nonane	8.83 ± 0.64	8.47 ± 0.56	8.65 ± 0.85
Cyclooctane	13.9 ± 0.3	12.8 ± 0.3	13.3 ± 0.4
2,2–Dimethylbutane	1.72 ± 0.03	1.69 ± 0.01	1.71 ± 0.03
2,2–Dimethylpentane	2.99 ± 0.06	2.96 ± 0.02	2.97 ± 0.06
2,2–Dimethylhexane	4.32 ± 0.09	4.28 ± 0.03	4.30 ± 0.09
2,2,4–Trimethylpentane	3.20 ± 0.08	3.19 ± 0.03	3.20 ± 0.09
2,2,3,3–Tetramethylbutane	0.66 ± 0.04	0.73 ± 0.03	0.70 ± 0.05
Benzene	0.95 ± 0.01	0.90 ± 0.01	0.92 ± 0.01
Toluene	7.09^a	6.52 ± 0.07	6.81 ± 0.07
Ethylbenzene	7.60 ± 0.35	7.41 ± 0.18	7.51 ± 0.39
p–Xylene	18.7 ± 0.6	17.3 ± 0.6	18.0 ± 0.85
o–Xylene	17.6 ± 1.1	16.3 ± 1.0	16.9 ± 1.49

[a] The Arrhenius expression leads to k (toluene) = 7.09 × 10^{-12} cm^3 s^{-1} at 248K [15]

[b] The Arrhenius expression leads to k (n–pentane) = 2.93 × 10^{-12} cm^3 s^{-1} at 248K [16]

Table S3 Arrhenius parameters A and B corresponding to the equation $k_{OH} = A\,e^{(-B/T)}$.

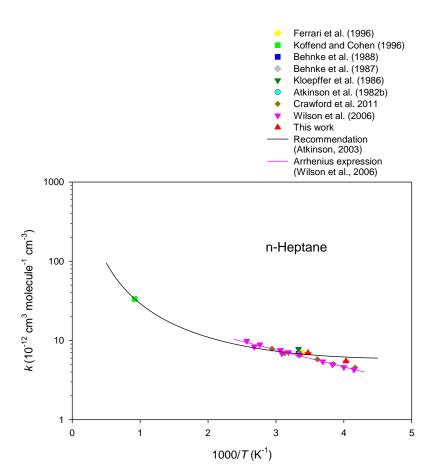|	$\ln(A/\mathrm{cm}^3\ \mathrm{s}^{-1})$	B/K
o–Xylene	-25.8 ± 0.4	-203 ± 126
p–Xylene	-25.3 ± 0.4	-62 ± 116
Ethylbenzene	-25.7 ± 0.5	-8 ± 135

Figure S6. Arrhenius plots of the rate constant for the reaction of OH radicals with *n*–heptane.

For *n*–heptane, our data differs from both the measurements from Crawford et al. and Wilson et al. In order to explain the discrepancy, we recalculate the rate constant by using *n*–butane, *n*–pentane and *n*–hexane as reference compounds respectively. The calculated rate constant decrease with increasing CH$_2$ chains: 7.00 ±0.19, 6.32 ±0.14 and 5.47 ±0.01 (in unit ×10^{-12} cm^3 molecule^{-1} s^{-1}) respectively. When using *n*–hexane alone as a reference compound, a lower reaction rate constant for *n*–heptane is obtained and it is very close to the data from Crawford et al. and Wilson et al. (figure S6). The understanding of temperature–dependence of *n*–pentane is more comprehensive, therefore, we choose *n*–pentane as our reference compound.

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