

Reactions of NO₃ with Aromatic Aldehydes: Gas Phase Kinetics and Insights into the Mechanism of the Reaction

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1. Error analysis

The quoted uncertainties in $\frac{k}{k_{ref}}$ ratios were estimated as follows: (1) The standard deviations of the least-squares fits of plots of $\ln\frac{[aromatic\ aldehyde]_0}{[aromatic\ aldehyde]_t} - k_d * t$ against $\ln\frac{[reference]_0}{[reference]_t} - k_d * t$ were calculated and twice this value was used; (2) the weighted average and error of repeated sampling was calculated using Eq.S2 and Eq.S3; (3) the total error in $\frac{k}{k_{ref}}$ was obtained by multiplying the computed error by factor of 2.9 (according to the Student *t*-distribution contribution) to account for the limited number of measurements.

The overall uncertainties for rate coefficients using the following propagation of uncertainty:

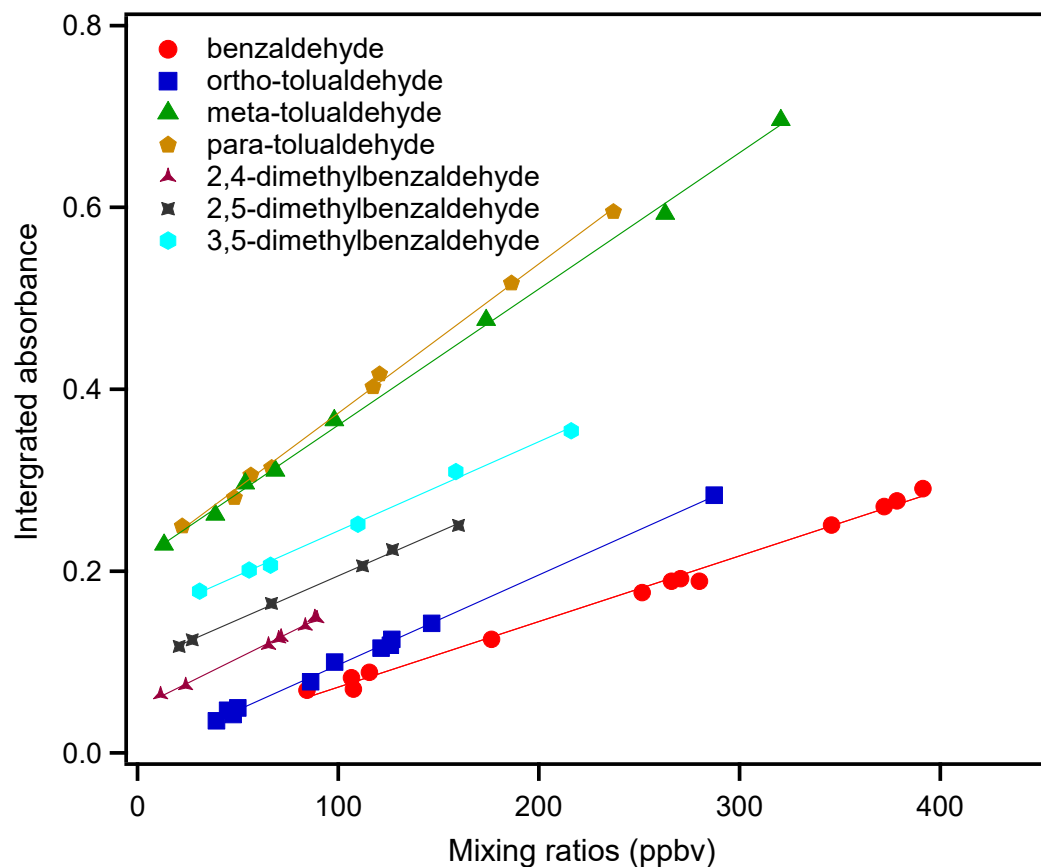
$$35 \quad \frac{k}{k_{ref}} k_{ref} \sqrt{\left[\frac{\sigma_{k_{ref}}}{k_{ref}}\right]^2 + \left[\frac{\sigma_{\frac{k}{k_{ref}}}}{\frac{k}{k_{ref}}}\right]^2} \quad \text{Eq.S1}$$

The weighted average is given by:

$$k_{average} = (w_1 k_1 + w_2 k_2 + \dots) / (w_1 + w_2 + \dots), \text{ where } w = 1/\sigma^2, \text{ etc.} \quad \text{Eq.S2}$$

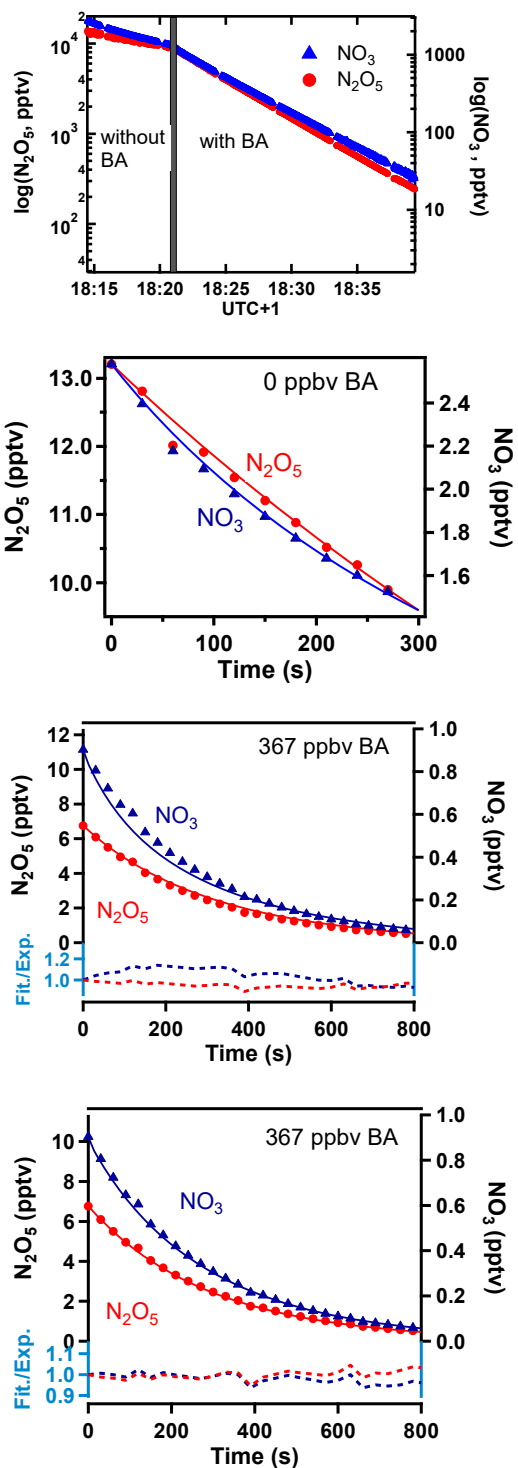
The error in this average, $\sigma_{average}$, is given by:

$$40 \quad \sigma_{av} = \left(\frac{1}{\sigma_1^2} + \frac{1}{\sigma_2^2} + \dots\right)^{-0.5} \quad \text{Eq.S3}$$



45 **Figure S1.** Calibration curve for studied aromatic aldehydes. Plots of the integrated absorbance (shown in Table S1) as a function of the mixing ratio in the chamber determined by manometric measurements for the various aldehydes noted in the legend. The data were fitted using a linear least-squares algorithm, assuming that the intercepts are zero. The plots are displaced vertically for the sake of clarity.

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55 **Figure S2** Observed (data points) and simulated (lines) profiles of N_2O_5 and NO_3 as functions
of reaction time for the reaction of NO_3 with benzaldehyde. The dashed lines in the bottom
panels show the ratio between simulated and observed values (Fit./Exp.). Mixing ratios of
benzaldehyde are shown in each panel. The first panel is the time profile on a log scale. The
60 data in the second panel was used to determine the wall loss of N_2O_5 and NO_3 . The simulations
in the third panel did not include subsequent reactions of the products of the NO_3 reaction. The
data in the bottom panel included all possible subsequent reactions (shown in Table S4). It
shows that the subsequent reactions do contribute to the long-term profiles.

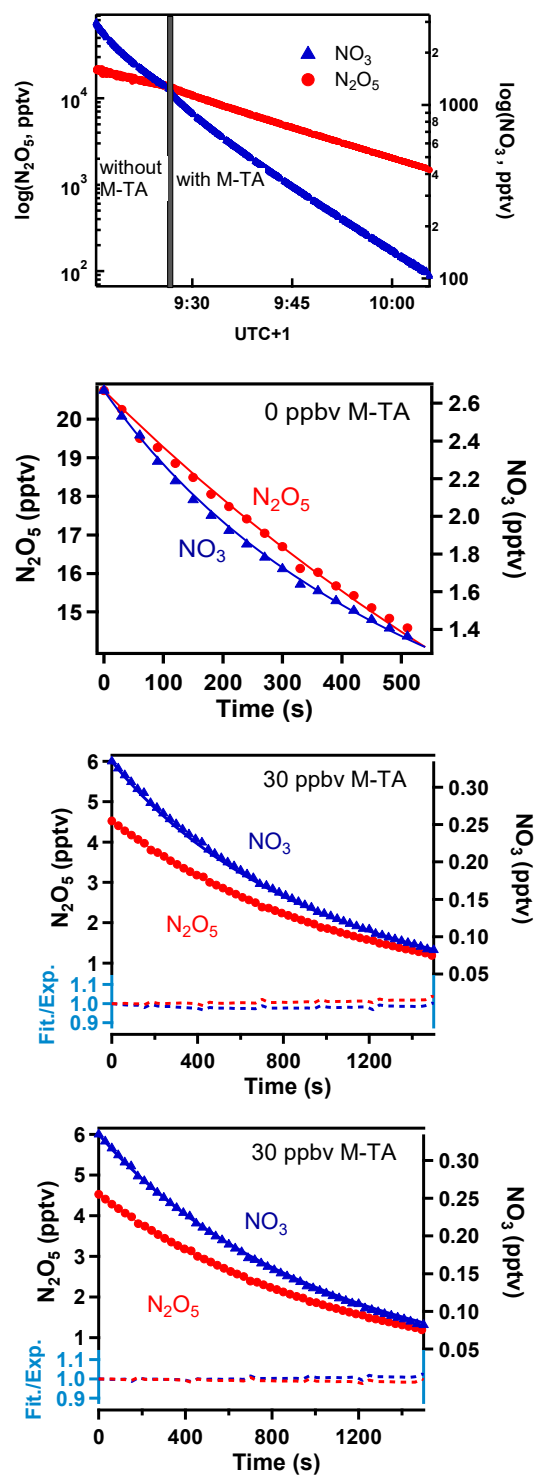
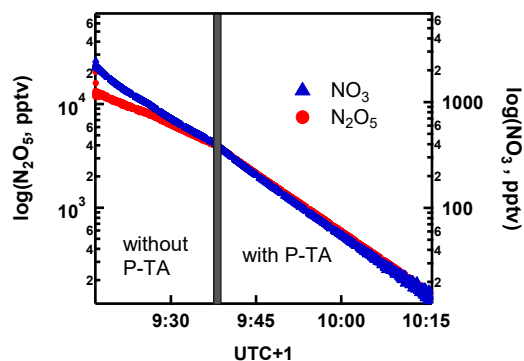
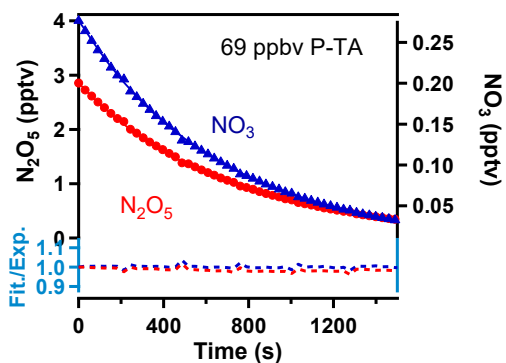
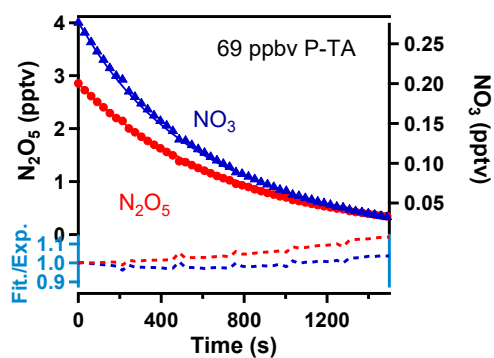
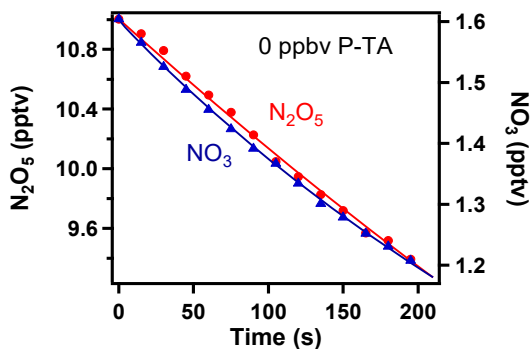


Figure S3 Observed (data points) and simulated (lines) profiles of N_2O_5 and NO_3 as functions of reaction time for the reaction of NO_3 with m-tolualdehyde. The dash lines in the bottom panels show the ratio between simulated and observed values (Fit./Exp.). Mixing ratios of benzaldehyde are shown in each panel. The first panel is the time profile on a log scale. The data in the second panel was used to determine the wall loss of N_2O_5 and NO_3 . The simulations in the third panel did not include subsequent reactions of the products of the NO_3 reaction. The data in the bottom panel included all possible subsequent reactions (shown in Table S4). It shows that the subsequent reactions do contribute to the long-term profiles.

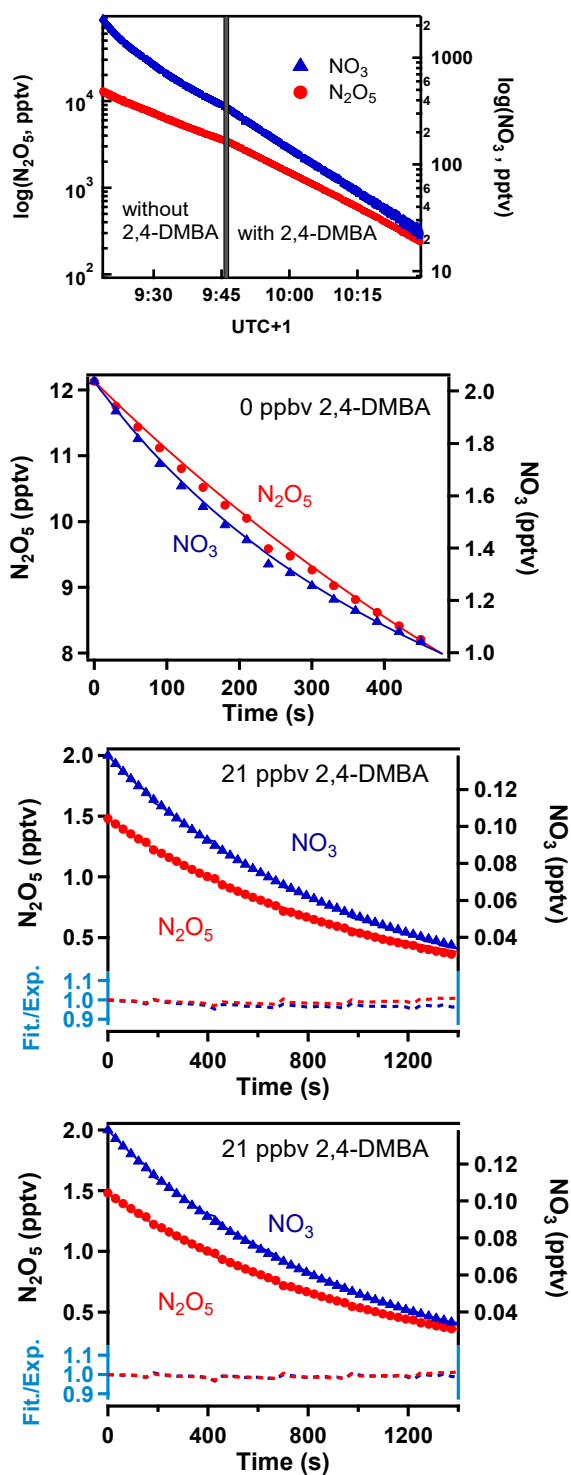


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80 **Figure S4** Observed (data points) and simulated (lines) profiles of N_2O_5 and NO_3 as functions of reaction time for the reaction of NO_3 with p-tolualdehyde. The dashed lines in the bottom two panels show the ratio between simulated and observed values (Fit./Exp.). Mixing ratios of benzaldehyde are shown in each panel. The first panel is the time profile on a log scale. The data in the second panel was used to determine the wall loss of N_2O_5 and NO_3 . The simulations in the third panel did not include subsequent reactions of the products of the NO_3 reaction. The data in the bottom panel included all possible subsequent reactions (shown in Table S4). It shows that the subsequent reactions do contribute to the long-term profiles.

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Figure S5 Observed (data points) and simulated (lines) profiles of N_2O_5 and NO_3 as functions of reaction time for the reaction of NO_3 with 2,4-dimethyl benzene. The dashed lines in the bottom two panels show the ratio between simulated and observed values (Fit./Exp.). Mixing ratios of benzaldehyde are shown in each panel. The first panel is the time profile on a log scale. The data in the second panel was used to determine the wall loss of N_2O_5 and NO_3 . The simulations in the third panel did not include subsequent reactions of the products of the NO_3 reaction. The data in the bottom panel included all possible subsequent reactions (shown in Table S4). It shows that the subsequent reactions do contribute to the long-term profiles.

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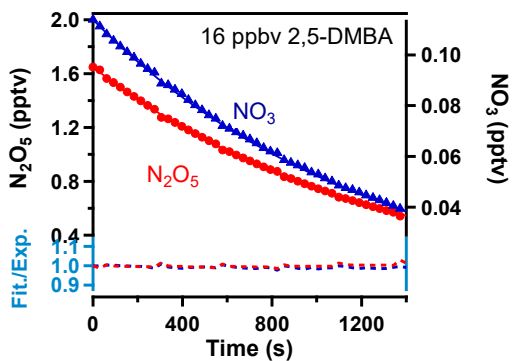
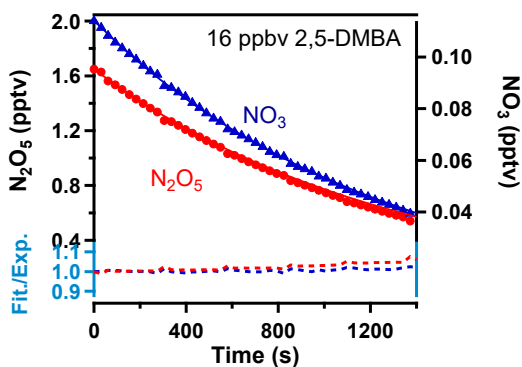
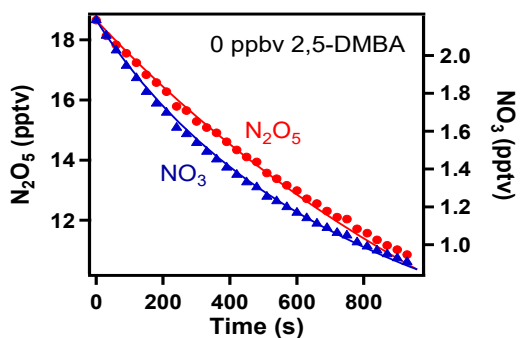
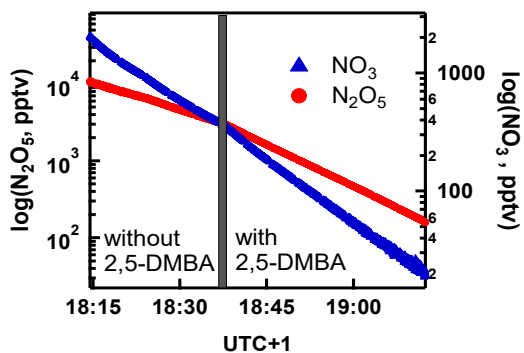
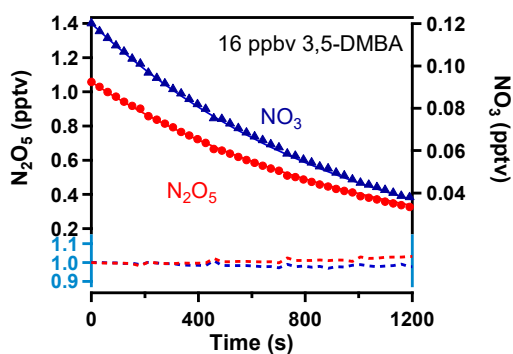
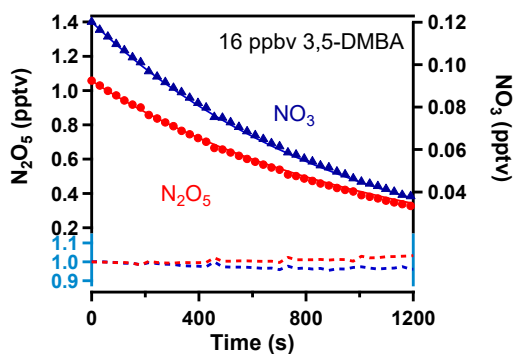
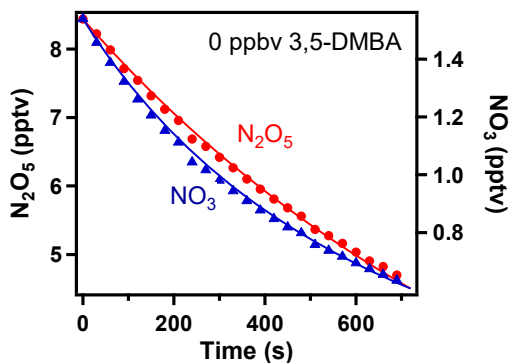
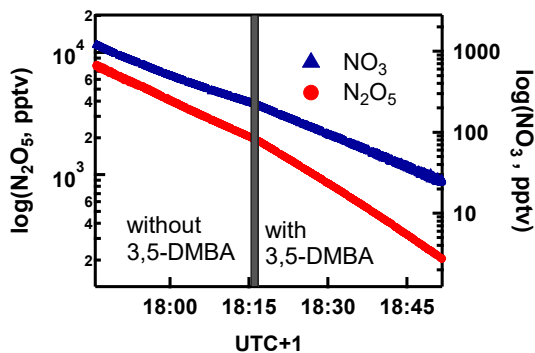
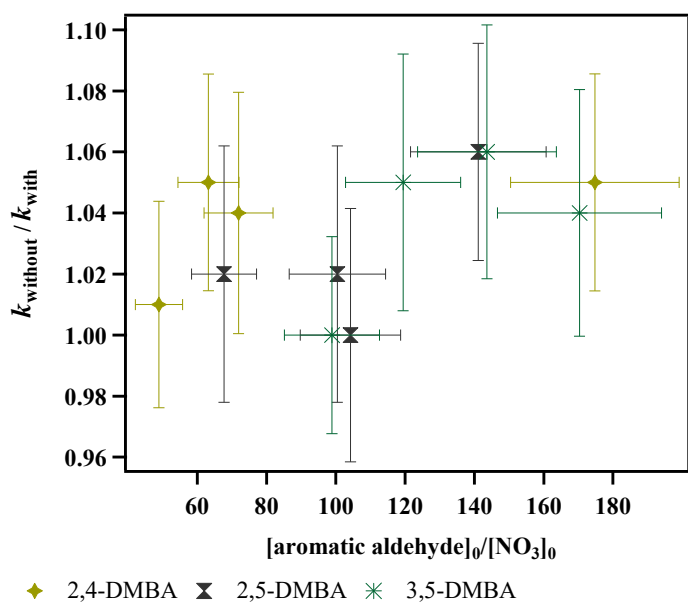
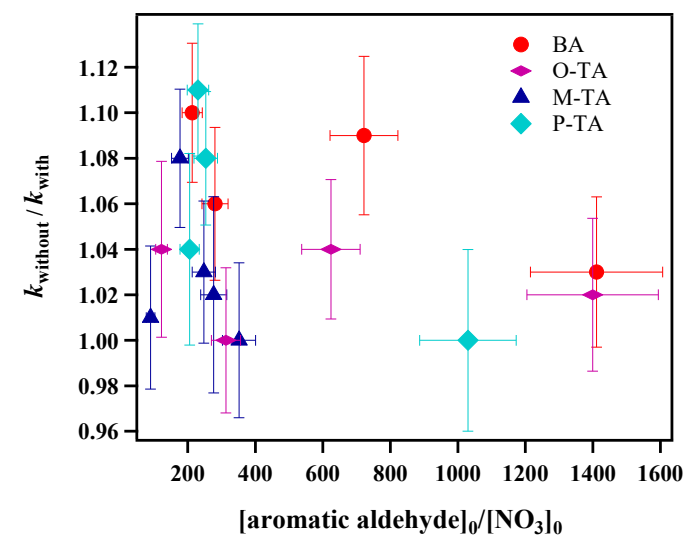


Figure S6 Observed (data points) and simulated (lines) profiles of N_2O_5 and NO_3 as functions of reaction time for the reaction of NO_3 with 2,5-dimethyl benzene. The dashed lines in the bottom two panels show the ratio between simulated and observed values (Fit./Exp.). Mixing ratios of benzaldehyde are shown in each panel. The first panel is the time profile on a log scale. The data in the second panel was used to determine the wall loss of N_2O_5 and NO_3 . The simulations in the third panel did not include subsequent reactions of the products of the NO_3 reaction. The data in the bottom panel included all possible subsequent reactions (shown in Table S4). It shows that the subsequent reactions do contribute to the long-term profiles.



115 **Figure S7** Observed (data points) and simulated (lines) profiles of N_2O_5 and NO_3 as functions
of reaction time for the reaction of NO_3 with 3,5-dimethyl benzene. The dashed lines in the
bottom two panels show the ratio between simulated and observed values (Fit./Exp.). Mixing
ratios of benzaldehyde are shown in each panel. The first panel is the time profile on a log scale.
The data in the second panel was used to determine the wall loss of N_2O_5 and NO_3 .
120 The simulations in the third panel did not include subsequent reactions of the products of the NO_3
reaction. The data in the bottom panel included all possible subsequent reactions (shown in
Table S4). It shows that the subsequent reactions do contribute to the long-term profiles.



125 **Figure S8** The ratio of rate coefficients without accounting for secondary reactions to that accounting for secondary reactions (using the reactions in Table S4) versus the ratio of initial aromatic aldehyde and NO₃ concentrations.

130 **Table S1.** List of specific masses monitored to detect various aromatic aldehydes using the PTR-TOF-MS and detection sensitivities and FTIR with the spectra range.

Aromatic aldehydes	PTR-TOF-MS		FTIR
	Mass charge ratio.H ⁺ (m/z)	detection sensitivity (ncps/ppbv)	wavenumber (cm ⁻¹)
benzaldehyde	107.049	96.51±3.53	2760-2660
ortho-tolualdehyde	121.065	96.81±2.17	2780-2660
meta-tolualdehyde	121.065	128.76±3.42	2780-2660
para-tolualdehyde	121.065	135.02±1.78	2780-2660
2,4-dimethyl benzaldehyde	135.081	84.97±2.54	2780-2660
2,5-dimethyl benzaldehyde	135.081	79.19±2.47	2780-2660
3,5-dimethyl benzaldehyde	135.081	89.34±2.21	2780-2660

Table S2. The experimental conditions and rate constants for the reactions of aromatic aldehydes with NO₃ radical by relative method using methyl methacrylate (MMA) as reference. Aromatic aldehyde includes benzaldehyde (BA), o-tolualdehyde (O-TA), m-tolualdehyde (M-TA), p-tolualdehyde (P-TA), 2,4-dimethyl benzaldehyde (2,4-DMBA), 2,5-dimethyl benzaldehyde (2,5-DMBA) and 3,5-dimethyl benzaldehyde (3,5-DMBA).

Aromatic aldehydes	[Aromatic aldehydes] (10 ¹² molecule cm ⁻³)	ref ^a	no of experiments	$\frac{k}{k_{ref}} \pm error$ ^b	$k_{RR} \pm 2\sigma$ (×10 ⁻¹⁵ cm ³ molecule ⁻¹ s ⁻¹) ^c
BA	3.3-4.5	MMA	2	0.93±0.09	2.8±0.4
O-TA	2.2-3.4	MMA	2	2.85±0.18	8.5±1.1
M-TA	1.0-2.1	MMA	2	1.66±0.12	5.0±0.7
P-TA	2.5-3.4	MMA	2	1.71±0.09	5.1±0.7
2,4-DMBA	2.0-2.5	MMA	2	5.29±0.35	15.8±2.1
2,5-DMBA	1.6-2.3	MMA	2	4.42±0.22	13.2±1.7
3,5-DMBA	0.9-1.7	MMA	2	2.12±0.07	6.3±0.8

^a k_{ref+NO_3} as: $k_{(MMA)} = (2.98 \pm 0.35) \times 10^{-15}$ (Zhou et al., 2017)

^b The errors estimated as detailed above.

^c the uncertainties for k include the precision of our measured values and the quoted uncertainties in the rate constant of references by using Eq.S1 in quadrature.

Table S3 The experimental conditions and the expected rate constants for the reaction of benzaldehyde (BA), o-tolualdehyde (O-TA), m-tolualdehyde (M-TA), p-tolualdehyde (P-TA), 2,4-dimethyl benzaldehyde (2,4-DMBA), 2,5-dimethyl benzaldehyde (2,5-DMBA) and 3,5-dimethyl benzaldehyde (3,5-DMBA) with NO₃ radical by absolute method using CRDS and Box model.

VOC	Initial mixing ratio of reactants (molecule cm ⁻³)				k ($\times 10^{-15}$ cm ³ molecule ⁻¹ s ⁻¹)		
	[VOC] ₀ ($\times 10^{12}$)	[NO ₃] ₀ ($\times 10^9$)	[N ₂ O ₅] ₀ ($\times 10^{10}$)	[NO ₂] ₀ ($\times 10^{11}$)	k_{aro1}^a	k_{aro2}^b	k_{AR}^c
BA	9.1	6.4	8.5	3.1	2.2±0.1	2.1±0.1	
	8.6	11.9	9.3	2.0	2.7±0.1	2.5±0.1	
	5.4	19.1	12.2	1.8	3.3±0.1	3.1±0.1	
	4.9	22.8	18.1	2.3	2.3±0.1	2.1±0.1	
				Average ^d	2.4±0.3	2.3±0.3	2.3±0.4
O-TA	2.7	4.3	5.6	3.3	8.5±0.2	8.2±0.2	
	1.5	5.9	6.3	2.2	9.4±0.2	9.3±0.2	
	3.4	27.9	36.5	3.9	9.9±0.3	9.5±0.3	
	3.1	9.9	15.0	4.5	9.8±0.2	9.8±0.2	
				Average ^d	9.3±0.5	9.1±0.5	9.1±1.2
M-TA	0.7	8.2	11.1	3.2	5.0±0.1	4.9±0.1	
	0.9	3.6	2.5	1.9	5.4±0.1	5.3±0.1	
	1.3	4.6	8.8	4.6	4.4±0.1	4.3±0.1	
	4.7	26.4	45.6	3.5	4.5±0.1	4.2±0.1	
	4.2	12.0	22.4	3.8	5.1±0.1	5.1±0.1	
			Average ^d	4.8±0.4	4.7±0.4	4.7±0.6	
P-TA	1.7	6.8	7.0	2.4	5.1±0.1	4.7±0.1	
	3.1	3.0	7.8	6.1	5.2±0.1	5.2±0.1	
	8.6	37.4	26.4	1.9	5.6±0.1	5.0±0.1	
	4.1	20.1	11.0	1.2	4.4±0.1	4.2±0.1	
				Average ^d	5.1±0.4	4.8±0.4	4.8±0.6
2,4-DMBA	0.5	3.0	3.4	2.7	16.9±0.5	16.1±0.5	
	0.2	3.4	3.6	2.6	17.6±0.5	17.4±0.5	
	1.4	22.2	21.6	2.8	15.1±0.4	14.4±0.4	
	1.2	16.3	18.9	3.5	12.9±0.4	12.4±0.4	
				Average ^d	15.1±0.7	14.6±0.7	14.6±2.0
2,5-DMBA	0.3	2.8	4.1	3.5	12.2±0.4	12.2±0.4	
	0.4	2.9	2.5	2.1	12.3±0.3	11.6±0.3	
	2.2	32.7	30.5	2.7	12.9±0.4	12.7±0.4	
	1.9	19.0	22.2	3.4	12.9±0.4	12.7±0.4	
				Average ^d	12.5±0.6	12.2±0.7	12.2±1.7
3,5-DMBA	0.3	3.0	2.6	2.1	6.6±0.2	6.6±0.2	
	0.4	2.3	2.1	2.2	6.6±0.2	6.4±0.2	
	3.9	27.4	18.2	1.9	6.8±0.2	6.4±0.2	
	3.6	30.1	26.3	2.0	5.3±0.2	5.1±0.2	
				Average ^d	6.3±0.5	6.1±0.4	6.1±0.8

^a The calculated values do not account for the secondary reactions listed in Table S4. Quoted errors are at the 95% confidence level based on the precision of the fitting.

^b The calculated values include the contributions of the secondary reactions listed in Table S4.
150 Quoted errors are at the 95% confidence level based on the precision of the fitting.

^c The quoted errors include estimated systematic errors and the Student t-distribution contribution due to a limited number of measurements.

^d Weighted average and error of repeated sampling was calculated using Eq.S2 and Eq.S3.

Table S4. Reaction scheme for NO₃ reacting with aromatic aldehydes in the presence of O₂ and nitrogen oxides that were included in simulating the temporal profiles of NO₃ and N₂O₅, and the yield of BAPAN.

Reactions	Rate coefficients 298 K, 1 bar air (cm ³ molecule ⁻¹ s ⁻¹ or s ⁻¹)	Reference
aromatic aldehydes + NO ₃ $\xrightarrow{k_x}$ PhCOO ₂ + HNO ₃	k _x (k ₁ -k ₇)	this work
NO ₃ +NO ₂ $\xrightarrow{k_9}$ N ₂ O ₅	1.35×10 ⁻¹²	a
N ₂ O ₅ $\xrightarrow{k_{10}}$ NO ₃ +NO ₂	0.04169	a
NO ₃ $\xrightarrow{k_{11}}$ loss	k ₁₀	b
N ₂ O ₅ $\xrightarrow{k_{12}}$ loss	K ₁₁	b
PhCOO ₂ + NO ₂ $\xrightarrow{k_{13}}$ PhCOO ₂ NO ₂	1.10×10 ⁻¹¹	c
PhCOO ₂ NO ₂ $\xrightarrow{k_{14}}$ PhCOO ₂ + NO ₂	3.18×10 ⁻⁴	c
PhCOO ₂ + NO ₃ $\xrightarrow{k_{15}}$ PhCOO + NO ₂ +O ₂		
Dialog to CH ₃ COO ₂	3.20×10 ⁻¹²	d
PhCOO ₂ + PhCOO ₂ $\xrightarrow{k_{16}}$ 2PhCOO+O ₂	1.5×10 ⁻¹¹	e
PhCOO $\xrightarrow{k_{17}}$ Ph+CO ₂		
Dialog to CH ₃ COO	1.0×10 ⁸	f
Ph+O ₂ $\xrightarrow{k_{18}}$ PhO ₂	1.8×10 ⁻¹¹	g
PhO ₂ +PhO ₂ $\xrightarrow{k_{19}}$ 2PhO	5.0×10 ⁻¹²	e
PhO ₂ +PhCOO ₂ $\xrightarrow{k_{20}}$ PhO+ PhCOO	1.0×10 ⁻¹¹	e
PhO+PhO ₂ $\xrightarrow{k_{21}}$ Ph ₂ O	5.0×10 ⁻¹²	e
PhO+PhO $\xrightarrow{k_{22}}$ Ph ₂ O ₂	1.49×10 ⁻¹¹	h
PhO+PhCOO ₂ $\xrightarrow{k_{23}}$ Ph ₂ CO+O ₃	2.0×10 ⁻¹¹	e
Ph+Ph $\xrightarrow{k_{24}}$ Ph ₂	1.91×10 ⁻¹¹	i

$\text{PhO}_2 + \text{NO}_2 \xrightarrow{k_{25}} \text{PhO}_2\text{NO}_2$	1.1×10^{-11}	c
$\text{PhO} + \text{NO}_2 \xrightarrow{k_{26}} \text{PhONO}_2$	2.10×10^{-12}	c

^a (J. B. Burkholder et al., 2015)

^b (Derived from the first period of the experiments: observation in the absence of aromatic aldehyde)

160 ^c (Caralp et al., 1999)

^d (Orlando and Tyndall, 2012)

^e (Roth et al., 2010)

^f (Hasson et al., 2012)

^g (Yu and Lin, 1994)

165 ^h (Tao and Li, 1999)

ⁱ (Park and Lin, 1997)

170 **Table S5** Experimental results of this study compared with those from the literature for the reactions of NO₃ radical with benzaldehyde (BA), o-tolualdehyde (O-TA), m-tolualdehyde (M-TA), p-tolualdehyde (P-TA), 2,4-dimethylbenzaldehyde (2,4-DMBA), 2,5-dimethylbenzaldehyde (2,5-DMBA) and 3,5-dimethylbenzaldehyde (3,5-DMBA).

VOC	k ($\times 10^{-15}$ cm ³ molecule ⁻¹ s ⁻¹)	T (K)	Technique	Reference compound	Ref. ($\times 10^{-15}$ cm ³ molecule ⁻¹ s ⁻¹)	Ref.
BA	<8	300±1	relative	propene	7.90	Carter et al. 1981
	1.1±0.3	296±2	relative	propene	4.07	Atkinson et al. 1984
	2.6±0.1	296±2	relative	propene	9.50	Atkinson et al. 1991
	4.2±0.2	295±2	relative	tetrahydrofuran	4.90	Clifford et al. 2005
	4.5±0.3	295±2	relative	n-propyl ether	4.90	Clifford et al. 2005
	2.2±0.6	301±3	absolute			Bossmeyer et al. 2006
	2.8±1.0	298±1	relative	MMA	2.98±0.35	this work
	2.3±0.4	298±1	absolute			this work
	2.6±0.3^a	298±2				recommended
O-TA	9.3±0.3	295±2	relative	tetrahydrofuran	4.90	Clifford et al. 2005
	10.3±0.4	295±2	relative	n-propyl ether	4.90	Clifford et al. 2005
	8.5±1.6	298±1	relative	MMA	2.98±0.35	this work
	9.1±1.3	298±1	absolute			this work
		8.8±0.8^b	298±1			
M-TA	9.4±0.4	295±2	relative	tetrahydrofuran	4.90	Clifford et al. 2005
	9.6±0.4	295±2	relative	n-propyl ether	4.90	Clifford et al. 2005
	4.9±1.2	298±1	relative	MMA	2.98±0.35	this work
	4.6±0.7	298±1	absolute			this work
		4.8±0.5^b				
P-TA	8.4±0.7	295±2	relative	tetrahydrofuran	4.90	Clifford et al. 2005
	10.2±0.4	295±2	relative	n-propyl ether	4.90	Clifford et al. 2005
	5.0±1.2	297±1	relative	MMA	2.98±0.35	this work
	4.8±0.7	297±1	absolute			this work
		4.9±0.5^b				
2,4-DMBA	15.8±2.2	297±1	relative	MMA	2.98±0.35	this work
	14.6±2.0	297±1	absolute			this work
		15.1±1.4^b				
2,5-DMBA	13.2±1.9	297±1	relative	MMA	2.98±0.35	this work
	12.2±1.7	297±1	absolute			this work
		12.7±1.2^b				
3,5-DMBA	6.2±1.3	297±1	relative	MMA	2.98±0.35	this work
	6.1±0.9	297±1	absolute			this work
		6.2±0.6^b				

^a weighted average of Atkinson (1991), Bossmeyer et al. (2006) and this work including results of relative and absolute method.

^b values shown in Table 1.

Table S6. The initial concentration used in measuring the yield of BAPAN ($C_6H_5C(O)O_2NO_2$) in the reaction between benzaldehyde and NO_3 .

Exp.	[benzaldehyde] $\times 10^{13}$ molecule cm^{-3}	[NO_2] $\times 10^{13}$ molecule cm^{-3}	[N_2O_5] $\times 10^{13}$ molecule cm^{-3}
1	1.4	~0	0.1
2	1.3	~0	1.5
3	1.3	~0	5.8
4	0.9	~0	6.3
5	1.0	2.5	5.6
6	1.1	2.8	13.7
7	1.1	13.5	14.7
8	1.0	32.5	12.2

180

Table S7. Net C-H bond dissociation enthalpies (BDEs) in aromatic aldehydes and the standard enthalpies of formation of the parent molecules and related radicals at 298.15 K and 0 K using Active Thermochemical Tables (ATcT) Thermochemical Network ver. 1.122x.^a

Species name	Formula	BDE (kcal/mol)		$\Delta_f H^\circ$ (kcal/mol)	
		298.15 K	0 K	298.15 K	0 K
acetaldehyde	CH ₃ C(O)-H	89.28 ± 0.06	87.86 ± 0.06	-39.57 ± 0.06	-37.05 ± 0.06
acetyl	CH ₃ CO			-2.39 ± 0.07	-0.82 ± 0.07
benzaldehyde	C ₆ H ₅ C(O)-H	90.89 ± 0.20	89.41 ± 0.20	-8.98 ± 0.19	-4.72 ± 0.19
benzoyl	C ₆ H ₅ CO			29.81 ± 0.26	33.05 ± 0.26
ortho-tolualdehyde	o-CH ₃ C ₆ H ₄ C(O)-H	89.93 ± 0.27	88.56 ± 0.27	-15.99 ± 0.26	-10.68 ± 0.26
ortho-toluoyl	o-CH ₃ C ₆ H ₄ CO			21.84 ± 0.34	26.24 ± 0.34
meta-tolualdehyde	m-CH ₃ C ₆ H ₄ C(O)-H	90.85 ± 0.27	89.35 ± 0.27	-17.20 ± 0.29	-11.73 ± 0.29
meta-toluoyl	m-CH ₃ C ₆ H ₄ CO			21.54 ± 0.34	25.99 ± 0.34
para-tolualdehyde	p-CH ₃ C ₆ H ₄ C(O)-H	90.83 ± 0.27	89.31 ± 0.27	-17.42 ± 0.28	-11.92 ± 0.28
para-toluoyl	p-CH ₃ C ₆ H ₄ CO			21.32 ± 0.34	25.76 ± 0.34

^a The quoted uncertainties are the best estimates of the corresponding 95% confidence intervals. The uncertainties for BDEs are obtained by using the full covariance matrix. Note that the enthalpies of formation of the radicals are highly correlated to those of the parent molecules, and thus the uncertainties of BDEs are smaller than those that would be obtained by propagating in quadrature the individual uncertainties of the relevant enthalpies of formation.

190 **2. Correlation of the rate constants for reactions of NO₃ radical with those for the reactions of OH radicals**

Canosa-Mas et al. (1988) showed a good correlation between the reactivities of alkynes towards OH and NO₃ radicals and attributed electrophilic addition in both cases. Sabljic and Gusten (1990) found a correlation between the rate coefficients of NO₃ and OH radicals reaction
195 with 72 aliphatic compounds and benzene derivatives. Wayne et al. (1991) concluded that the general form of these correlations is a linear relationship between the logarithms of the rate constants for the reactions of NO₃ and those for the reactions of OH as a particular series of substrates:

$$\log(k_{\text{NO}_3}) = a \times \log(k_{\text{OH}}) + b$$

200 In their review, Wayne et al. (1991) reviewed updated rate coefficients (Atkinson, 1997; Atkinson et al., 1997, 1999) for reaction with OH and NO₃ radicals. D'Anna et al. (2001) developed the correlation lines for abstraction and addition. The correlation line for H-atom abstraction from saturated hydrocarbons was given by:

$$\log(k_{\text{NO}_3}) = (0.87 \pm 0.09) \times \log(k_{\text{OH}}) + (-6.0 \pm 1.0)$$

205 The correlation line for addition to unsaturated hydrocarbons is given by:

$$\log(k_{\text{NO}_3}) = (3.43 \pm 0.24) \times \log(k_{\text{OH}}) + (22.7 \pm 2.5)$$

The correlation lines (green) for H-atom abstraction from the saturated hydrocarbons are shown in Figure S9. The addition pathways for NO₃ and OH addition to olefins, aliphatic aldehydes, and the seven aromatic aldehydes obtained in this work are also shown in the figure. The
210 correlation line (black) of 15 aliphatic aldehydes is given by:

$$\log(k_{\text{NO}_3}) = (2.91 \pm 0.20) \times \log(k_{\text{OH}}) + (16.9 \pm 2.1);$$

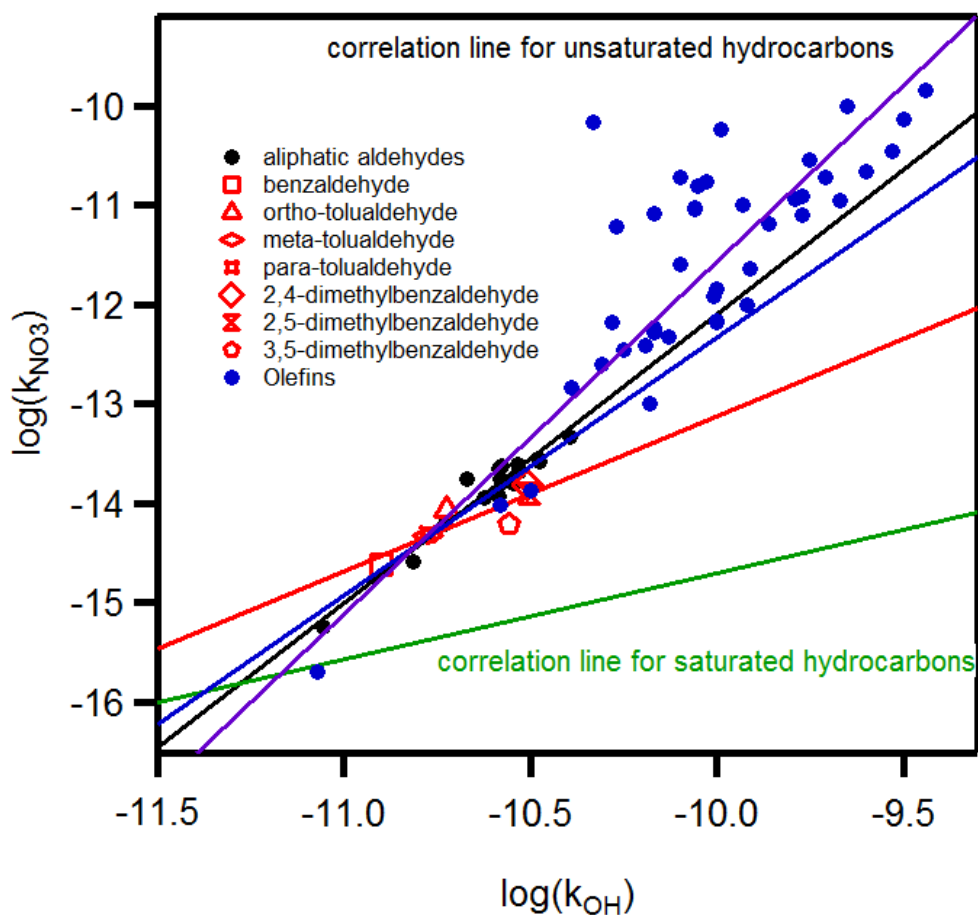
The correlation line (red line) of 7 studied aromatic aldehydes is given by:

$$\log(k_{\text{NO}_3}) = (1.56 \pm 0.38) \times \log(k_{\text{OH}}) + (2.44 \pm 4.08);$$

The correlation line (blue) of 15 aliphatic and 7 aromatic aldehydes together is given by:

215
$$\log(k_{\text{NO}_3}) = (2.60 \pm 0.23) \times \log(k_{\text{OH}}) + (13.65 \pm 2.45).$$

Figure S9 shows that the aromatic aldehydes fall close to the line for the addition line, suggesting that the OH and NO₃ reaction with aromatic aldehydes also proceed through an addition pathway.



220 **Figure S9** Linear free energy plot for the reactions of OH and NO₃ radicals with a series of 15
 aliphatic aldehydes, 7 aromatic aldehydes and 41 olefins. The correlation line (green line) for
 H-atom abstraction of saturated hydrocarbons is given by: $\log(k_{\text{NO}_3}) = (0.87 \pm 0.09) \times \log(k_{\text{OH}})$
 $+ (-6.0 \pm 1.0)$ and the correlation line (black line) of 15 aliphatic aldehydes is given by:
 $\log(k_{\text{NO}_3}) = (2.91 \pm 0.20) \times \log(k_{\text{OH}}) + (16.9 \pm 2.1)$; the correlation line (red line) of 7 studied
 225 aromatic aldehydes is given by: $\log(k_{\text{NO}_3}) = (1.56 \pm 0.38) \times \log(k_{\text{OH}}) + (2.44 \pm 4.08)$; the
 correlation line (blue line) of 15 aliphatic and 7 aromatic aldehydes is given by: $\log(k_{\text{NO}_3}) =$
 $(2.60 \pm 0.23) \times \log(k_{\text{OH}}) + (13.7 \pm 2.5)$; the correlation line (violet line) of 15 aliphatic
 aldehydes, 7 aromatic aldehydes and 41 olefins is given by: $\log(k_{\text{NO}_3}) = (3.54 \pm 0.19) \times$
 $\log(k_{\text{OH}}) + (23.9 \pm 1.9)$.

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