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Kinetics of the gas-phase reactions of OH and NO$_3$ radicals with aromatic aldehydes

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Abstract

Rate coefficients for the reactions of hydroxyl (OH) and nitrate (NO$_3$) radicals with benzaldehyde and the tolualdehydes have been determined at 295 ± 2 K and atmospheric pressure using the relative rate technique. Experiments were performed in atmospheric simulation chambers using gas chromatography for chemical analysis. The rate coefficients (in units of cm^3 molecule^{-1} s^{-1}) are:

Compound	k_{OH}	k_{NO_3}
Benzaldehyde	$(14.0 \pm 2.0) \times 10^{-12}$	$(4.3 \pm 0.3) \times 10^{-15}$
o-Tolualdehyde	$(20.4 \pm 2.3) \times 10^{-12}$	$(9.8 \pm 0.4) \times 10^{-15}$
m-Tolualdehyde	$(20.7 \pm 2.4) \times 10^{-12}$	$(9.5 \pm 0.4) \times 10^{-15}$
p-Tolualdehyde	$(20.5 \pm 2.2) \times 10^{-12}$	$(9.5 \pm 0.7) \times 10^{-15}$

The reactivity of the aromatic aldehydes is compared to other aromatic compounds and it is shown that, for the tolualdehydes, the OH and NO$_3$ rate coefficients do not depend on the position of the CH$_3$ substituent on the aromatic ring. The new data are used to show that the gas-phase reactivity of the aromatic aldehydes towards OH and NO$_3$ radicals follows a linear free energy relationship typical of addition reactions, although the net result is H-atom abstraction. The rate coefficient data are explained in terms of known mechanistic features of the reactions and simple theoretical calculations have been performed in an attempt to understand the observed trends in reactivity. The atmospheric implications are also discussed.
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Keywords: Aromatic aldehydes; Atmospheric degradation; OH radicals; NO$_3$ radicals; Kinetics

1. Introduction

The occurrence of aromatic aldehydes in the lower atmosphere is mainly linked to anthropogenic activity. They are emitted to the atmosphere as primary pollutants during fuel burning and solvent usage [1]. Benzaldehyde is used as a starting material in the manufacture of pharmaceuticals and pesticides and is also emitted naturally from various plants [2], whilst methylbenzaldehydes (tolualdehydes) are present in wood smoke [3]. Benzaldehyde, o-, m- and p-tolualdehyde are also formed in situ from the OH initiated oxidation of toluene, o-, m- and p-xylene,

respectively [4]. The aromatic aldehydes can undergo degradation in the atmosphere thus contributing to the formation of secondary pollutants such as ozone and nitrates, which are major constituents of air pollution in the boundary layer. In order to fully understand the environmental impact of the aromatic aldehydes, a detailed knowledge of the kinetics and mechanisms for their atmospheric degradation is required.

The major atmospheric loss processes for aromatic aldehydes are expected to be gas-phase reaction with OH and NO$_3$ radicals and photolysis by sunlight [1]. The relative contribution of these reactions to the atmospheric loss of the aromatic aldehydes is dependent on the magnitude of the rate coefficients for the reactions and the ambient concentrations of the radical species. To date, laboratory kinetic studies have largely focussed on benzaldehyde, with rate coefficients for the reaction with OH [5–9]

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and NO_3 [10–13] reported on several occasions. However, the reactions of the tolualdehydes with OH have only been studied once before [9] and no data concerning their reaction with NO_3 are available.

The aim of this work was to determine rate coefficients for the reaction of benzaldehyde and the tolualdehydes with OH and NO_3 radicals in order to assess the relative importance of these reactions as atmospheric loss processes. Simple theoretical calculations have also been performed in an attempt to understand the observed trends in reactivity of benzaldehyde and the tolualdehydes. Finally, the reactivity of the aldehydes is compared to other aromatic compounds and the results are interpreted in light of the current understanding of the atmospheric chemistry of aromatic compounds.

2. Experimental

Rate coefficients for the reactions of the aromatic aldehydes with OH and NO_3 at 295 ± 2 K and atmospheric pressure were determined using a relative rate method in which the decay rates of the compounds were measured relative to that of a reference organic compound. Experiments were performed in two atmospheric simulation chambers which were operated using purified air (non-methane-hydrocarbons <10 ppbV, NO_x <10 ppbV) and equipped with gas chromatography for chemical analysis.

The first chamber is a collapsible pillow-shaped FEP Teflon reaction vessel with a volume of about 350 L at atmospheric pressure. Four apertures sealed into the foil are used for the introduction and sampling of gases and vapours. The reactor is surrounded by eight lamps with $\lambda_{max} = 360$ nm (Philips TL05), and four lamps with $\lambda_{max} = 254$ nm (Philips TUV) arranged on different circuits to allow variation of light intensity and wavelength. Prior to addition of reactants the chamber was filled with 200 L of purified air and a gas chromatogram of the contents was taken to ensure that no impurities were present. The aldehydes and reference compounds were introduced into the reaction chamber using an inlet system in which weighed amounts of the substances were heated in a small flow of purified air. The inlet lines were also heated to avoid condensation of the semi-volatile compounds before entering the chamber. A scanning mobility particle sizer (TSI Instruments Model 3936L10) was used to check that this method for introducing samples did not produce a significant amount of particles. The observed particle number concentrations were in the range 10–50 particles cm^{-3}, which is typical of background levels in the chamber and thus confirms the suitability of the sample introduction method.

The hydroxyl radical reactions were performed using the photolysis of methyl nitrite as the radical source:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO$$

$$HO_2 + NO \rightarrow NO_2 + HO$$
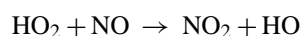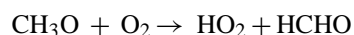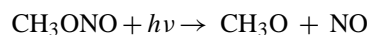
Measured amounts of methyl nitrite were flushed from a Pyrex bulb into the chamber by a stream of purified air. A gas chromatogram of the contents was taken to confirm the presence of CH_3ONO. The initial reactant concentrations in the chamber (in molecule cm^{-3}) were as follows: $[CH_3ONO] = 1.2 \times 10^{15}$ to 2.0×10^{15}, [aldehyde] $= 2.5 \times 10^{14}$ to 15.0×10^{14} and [reference] $= 2.5 \times 10^{14}$ to 15.0×10^{14}. The reactant mixtures were photolysed (3 TL05 lamps) for 1–2 min and a gas chromatograph of the chamber contents was taken. This photolysis-sampling procedure was repeated until around 30% depletion of the substrate and reference compound was achieved. Typically six to nine photolysis-sampling steps were carried out during each experiment. At least three experiments were carried out with each individual reference compound.

The nitrate radical reactions were performed using the reaction of NO_2 and O_3 as the radical source:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
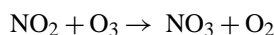
The reactant gases were flowed through a Pyrex tube and into the chamber containing the reactant and reference compounds. The flow rates of the gases were adjusted to ensure that an excess of NO_2 was present. Under these conditions NO_2 can also react with nitrate radicals to form N_2O_5 which acts a temporary reservoir of NO_3 through the following equilibrium:

$$NO_2 + NO_3 + M \leftrightarrow N_2O_5 + M$$

The initial reactant concentrations (in molecule cm^{-3}) were as follows: [aldehyde] $= 3.0 - 7.5 \times 10^{14}$ and [reference] $= 2.5 - 11.0 \times 10^{14}$. During each experiment, successive additions of NO_2 $(2.5 - 8.8 \times 10^{13}$ molecule $cm^{-3})$ and O_3 $(1.3 - 3.0 \times 10^{13}$ molecule $cm^{-3})$ were performed. The concentrations of the reactant and reference compounds were monitored by gas chromatography. Sampling was carried out approximately 8 min after the addition of NO_3 radicals and at further 8 min intervals. When the concentration of the organic compounds stabilized, thus indicating that the reaction was complete, another addition of NO_2 and O_3 was performed. Typically, six to nine additions were made in each experiment. At least three experiments were carried out with each individual reference compound.

The second chamber, which was used for supplementary OH radical experiments, has been described in detail elsewhere [14]. It is a cylinder consisting of a FEP foil tube (4.1 m long, 1.1 m diameter) closed at both ends by FEP foil covered aluminium plates. At atmospheric pressure the chamber has a volume of 3910 L and a volume to surface area ratio of ca. 0.24 m. The chamber is surrounded by 18 Philips TUV (40 W) lamps with an emission maximum at 254 nm and 18 Philips TL05 (40 W) lamps with an emission maximum at 360 nm. The procedure for the OH radical experiments was identical to that described above for the 350 L chamber. The initial reactant concentrations (in molecule cm^{-3}) were as follows: $[CH_3ONO] = 1.2 \times 10^{15}$ to 2.0×10^{15}, [aldehyde] $= 2.5 \times 10^{14}$ to 7.5×10^{14} and [reference] $= 2.5 \times 10^{14}$ to 7.5×10^{14}. The reactant mixtures were photolysed (six TL05 lamps) for 1–2 min and a gas chromatograph of the chamber contents was taken. This photolysis-sampling procedure was repeated six to nine times until around 30% depletion of the substrate and reference compounds was achieved.
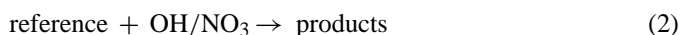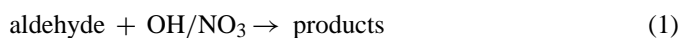
Before kinetic experiments were carried out, the possibility of wall loss and photolysis of the aromatic aldehydes were investigated. To check for wall loss, compounds were left in the chamber for up to 5 h and sometimes overnight. Gas chromatographic analysis was performed at approximately 8 min intervals to see if compounds were lost to the walls over time. Irradiation of the aldehydes in the absence of radical precursor was also carried out to ascertain the photostability of reactants. A 10-fold excess of *n*-butyl ether was added to the chamber to act as a scavenger for any OH radicals produced from the chamber walls. The TL05 lights were switched on for the same amount of time as in a relative rate experiment. The possible reactions of NO_2 and O_3 with the reference and reactant compounds were checked by adding these compounds separately into the chamber and monitoring the concentration of the hydrocarbons for several hours. In these tests, the loss of hydrocarbons was no greater than the wall loss, thus confirming that reaction of the reactant and reference compounds with NO_2 and O_3 are of negligible importance.

A high performance Varian GC-FID 3800 (Gas Chromatograph with flame ionisation detector), directly connected to the reaction chamber via a six-port gas sampling valve (Valco), was used for chemical analysis in the OH and NO_3 radical experiments. The valve is fitted with a 1 ml sampling loop and is equipped with a pneumatically controlled actuator to enable automatic injection of reaction mixtures onto the column. Chromatographic separation was achieved by using a CP-Sil5 capillary column (Varian, 30 m, 0.53 mm i.d., 5 μm film thickness). The column was operated using a flow rate of 5 ml min^{-1} and an initial oven temperature of 90 °C which was then increased to 140 °C after the elution of the reference compound. Chromatograms were recorded and analyzed using the Varian software. The relative concentrations of each compound were determined from peak area measurements during analyses.

All tolualdehydes and reference compounds used in this study were obtained from Aldrich Chemical Company (stated purities > 97%) and used without further purification. Methyl nitrite was synthesized following the method of Taylor et al. [15] and its purity checked by FTIR spectroscopy. Nitrogen dioxide (>98%) was obtained from BOC gases. Ozone was generated by passing oxygen through an ozone generator (Yanco GE60/FM5000).

3. Results

Rate coefficients for the reactions of the aromatic aldehydes with OH and NO_3 were determined by comparing the rates of decay of the reactant relative to that of selected reference compounds:

$$\text{aldehyde} + \text{OH/NO}_3 \rightarrow \text{ products} \tag{1}$$

$$\text{reference} + \text{OH/NO}_3 \rightarrow \text{ products} \tag{2}$$

Due to their low volatility, the aromatic aldehydes were also lost to the walls of the reactor via deposition:

$$\text{aldehyde} + \text{wall} \rightarrow \text{ products} \tag{3}$$

No wall deposition was observed for the reference compounds. Kinetic treatment of the reactions expressed in Eqs. (1)–(3) yields the following relationship:

$$\ln \frac{[\text{aldehyde}]_0}{[\text{aldehyde}]_t} - k_{\text{wall}}t = \frac{k_1}{k_2} \ln \frac{[\text{reference}]_0}{[\text{reference}]_t} \tag{I}$$

where k_1, k_2 and k_{wall} are the rate coefficients for reactions (1)–(3) and the subscripts 0 and t indicate concentrations at the start of the reaction and at time t, respectively.

The addition of NO_3 radical precursors results in a slight dilution of the concentration of reactant and reference compounds. However, the total volume of gas added in each experiment was less than 2 L, corresponding to about 0.6% and 0.05% of the volume in the 350 and 3910 L reaction chambers, respectively. Thus dilution is of negligible importance and for the sake of simplicity is not considered here.

o-Tolualdehyde, however, was found to be susceptible to photolysis by the lamps used to generate OH radicals.

$$o\text{-tolualdehyde} + h\nu \rightarrow \text{ products} \tag{4}$$
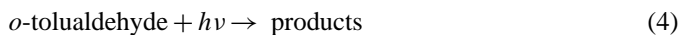
No photolysis was observed for benzaldehyde, *m*- and *p*-tolualdehyde or any of the reference compounds. Incorporating the photolysis of *o*-tolualdehyde into Eq. (I) yields the following relationship:

$$\ln \frac{[o\text{-tolualdehyde}]_0}{[o\text{-tolualdehyde}]_t} - k_{\text{wall}}t - k_p t_p = \frac{k_1}{k_2} \ln \frac{[\text{reference}]_0}{[\text{reference}]_t} \tag{II}$$

where k_p is the rate coefficient representing the photolysis of *o*-tolualdehyde. It should be noted that wall loss was occurring throughout the experiment whilst photolysis was only occurring when the lamps were switched on. As a result, a different timescale is required for the photolysis loss in Eq. (II), denoted by t_p.

For the reactions of NO_3 and OH with benzaldehyde, *m*- and *p*-tolualdehyde, plots in the form of Eq. (I) should yield a straight line with zero intercept and slope k_1/k_2. For *o*-tolualdehyde, Eq. (II) is appropriate for the OH experiments and Eq. (I) is appropriate for the NO_3 experiments, where no photolysis was occurring.

The concentrations of reactant and reference compounds were determined directly by gas chromatography. The rates of loss of the tolualdehydes to the walls of the chambers were determined by measuring the decay of the compounds over a period of at least 2 h prior to the start of every experiment. Values of $k_{\text{wall}} = 3.1 - 6.3 \times 10^{-6} \text{ s}^{-1}$ were obtained for benzaldehyde, *m*- and *p*-tolualdehyde in the 350 L chamber, which means that wall loss accounted for 4–10% of the overall decay of the compounds during OH and NO_3 experiments. The wall loss and photolysis rate coefficients for *o*-tolualdehyde in the 350 L chamber were $k_{\text{wall}} = 4.9 \times 10^{-6} \text{ s}^{-1}$ and $k_p = 5.1 \times 10^{-6} \text{ s}^{-1}$, accounting for 8% of the overall decay. In the 3910 L chamber, values of $k_3 = 2.0 \times 10^{-6}$ to $3.0 \times 10^{-6} \text{ s}^{-1}$ were obtained for benzaldehyde, *m*- and *p*-tolualdehyde, corresponding to 3–6.5% of the overall loss. The wall loss and photolysis rate coefficients for *o*-tolualdehyde in the 3910 L chamber were $k_{\text{wall}} = 2.3 \times 10^{-6} \text{ s}^{-1}$
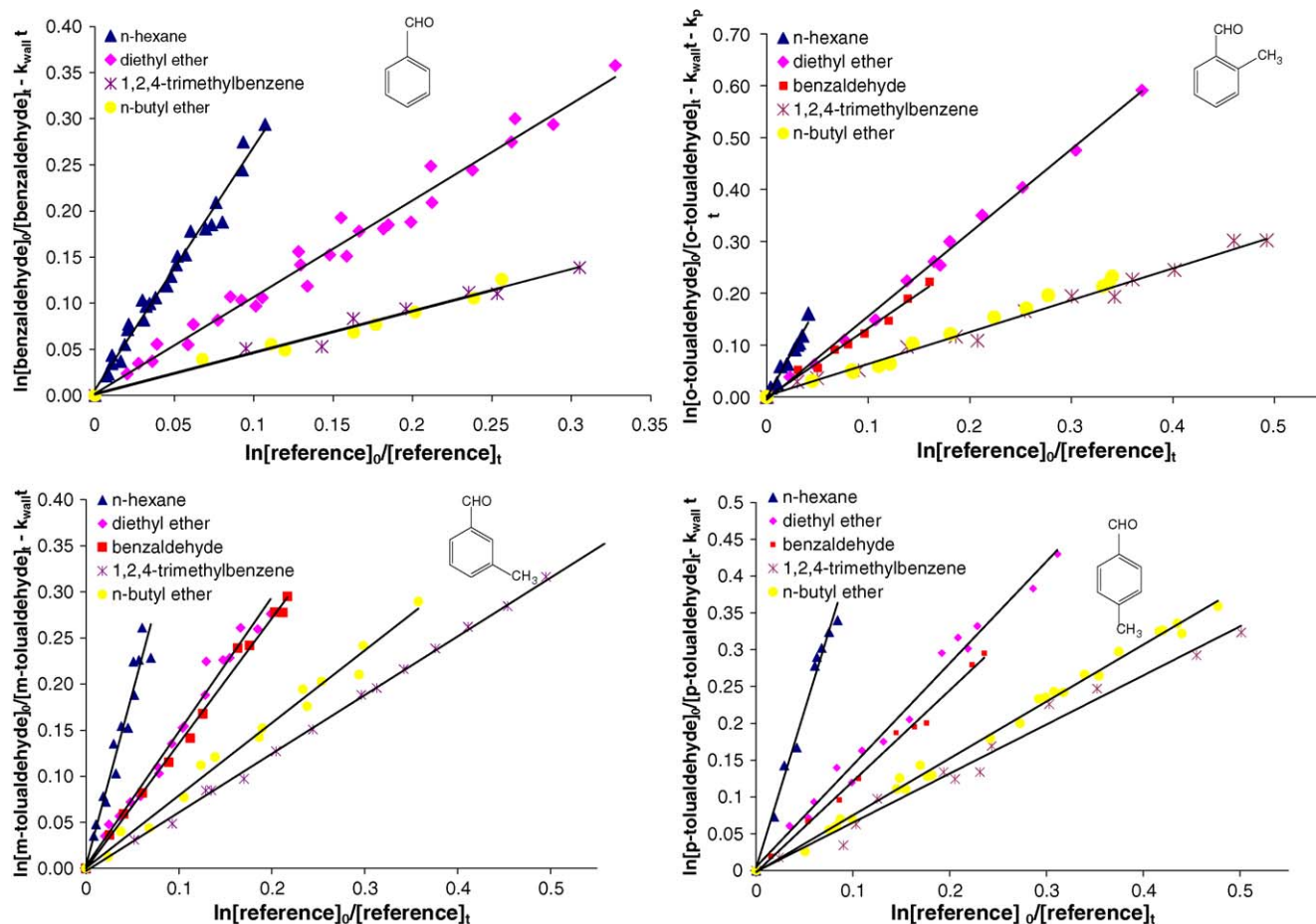
Fig. 1. Relative rate plots for the reaction of OH radicals with benzaldehyde, o-, m- and p-tolualdehyde at 295 ± 2 K.

and $k_p = 1.0 \times 10^{-5}\,\text{s}^{-1}$, accounting for 16% of the overall decay.

Data generated from the OH reactions were plotted in the form of Eqs. (I) or (II) and are shown in Fig. 1. Data generated from the NO$_3$ reactions were plotted in the form of Eq. (I) and are shown in Fig. 2. The plots show good linearity and have zero intercepts (within error). Rate coefficients for the reaction of OH and NO$_3$ radicals with the aromatic aldehydes (k_1) were calculated from the gradients of the plots (k_1/k_2). The reference compounds used in this study and their rate coefficients (k_2) for reaction with OH and NO$_3$ are shown in Tables 1 and 2,

respectively. A summary of the reactant concentrations, gradients (k_1/k_2) and obtained rate coefficients for the OH and NO$_3$ reactions are shown in Tables 3 and 4, respectively. In all experiments, the initial concentration of substrate and reference compounds were established to provide ratios of approximately 1:1, 1:2 and 2:1 as this range was expected to highlight the possibility that secondary reactions could also be contributing to the loss of reactants. The indicated errors on k_1 are twice the standard deviation arising from the least squares fit of the data and do not include an estimate of the error in the reference rate coefficients, k_2. The errors in k_2 may add a further 20% to the uncertainty of the rate coefficients reported in this relative rate study [1,13,17].

Table 1
Reference compounds used in the OH radical experiments and their rate coefficients for reaction at 295 ± 2 K

Reference compound	k_{OH}[a]	Reference
n-Butyl ether	28.8	[1]
Tetrahydrofuran	17.4	[16]
1,2,4-Trimethylbenzene	32.5	[17]
Diethyl ether	13.6	[18]
n-Hexane	5.4	[19]
Benzaldehyde	14.0	This work[b]

[a] In units of $\times 10^{-12}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$.
[b] Value obtained from experiments performed in the 3910 L reaction chamber.

Table 2
Reference compounds used in the NO$_3$ radical experiments and their rate coefficients for reaction at 295 ± 2 K

Reference compound	k_{NO_3}[a]	Reference
Tetrahydrofuran	4.9	[20]
n-Propyl ether	4.9	[21]
Benzaldehyde	4.3	This work[b]

[a] In units of $\times 10^{-15}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$.
[b] Value obtained from experiments performed in the 350 L reaction chamber.
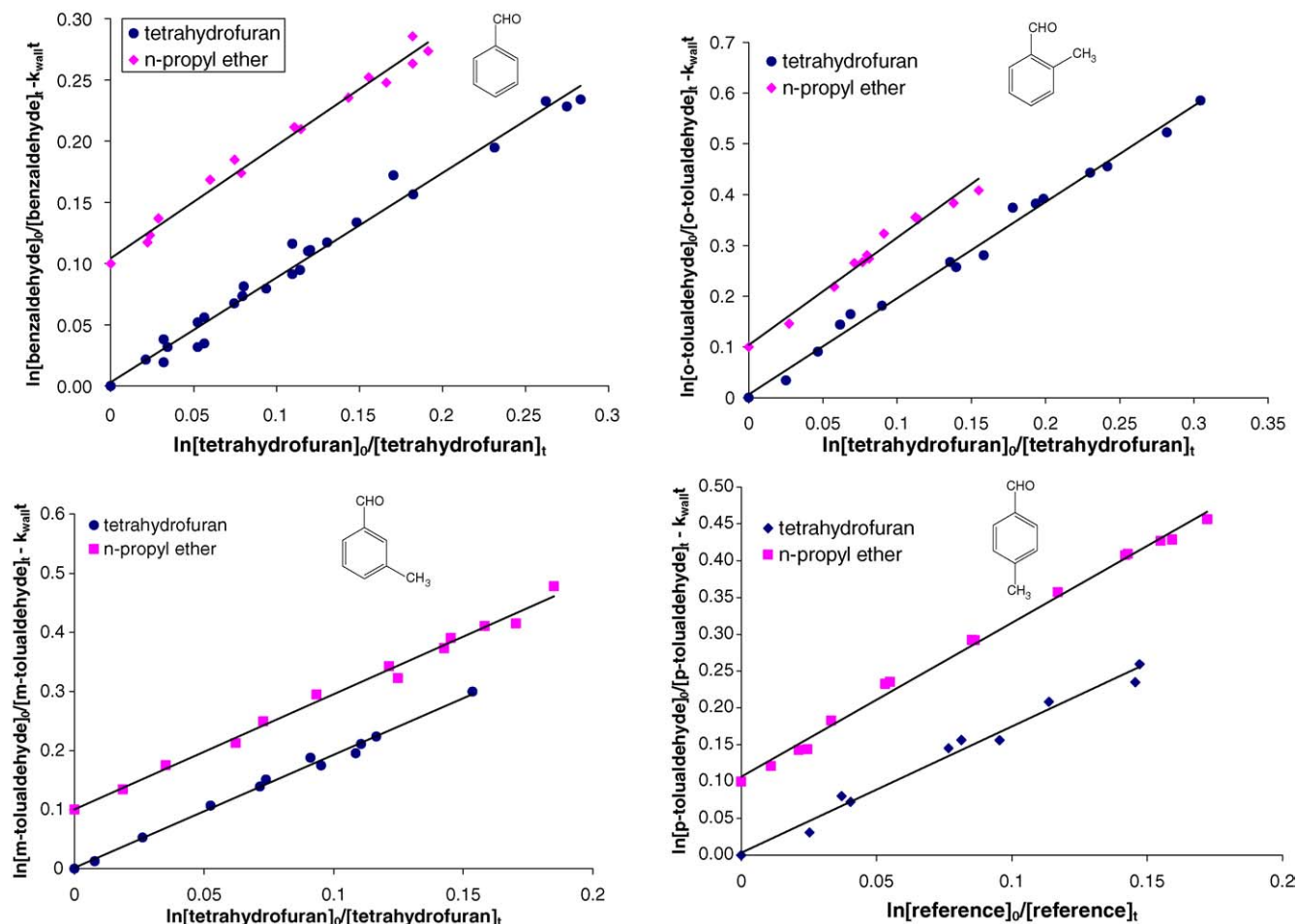
Fig. 2. Relative rate plots for the reaction of NO_3 radicals with benzaldehyde, *o*-, *m*- and *p*-tolualdehyde at 295 ± 2 K. For reasons of clarity, the data for *n*-propyl ether have been displaced vertically by 0.1 units.

4. Discussion

4.1. OH radical kinetics

The rates of reaction of OH with benzaldehyde and the tolu-aldehydes at 295 ± 2 K were measured against at least five different reference compounds and in two reaction chambers. The average values of the rate coefficients are compared to the available literature data in Table 5. All previously reported rate coefficients for benzaldehyde and the tolualdehydes were determined using the relative rate method.

The five relative rate coefficients obtained in this study for the reaction of OH with benzaldehyde are in good agreement with each other and those previously reported in the literature. In fact, all the values listed in Table 5 are close to the value of k_{OH}(benzaldehyde) $= 12.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} recommended by Calvert et al. [4] and are well within the estimated overall uncertainty of $\pm 25\%$. The rate coefficients obtained in this study for the reaction of OH with the tolualdehydes are also compared to those previously reported in the literature in Table 5. There is good agreement between the values obtained in this work using the different reference compounds. All rate coefficients agree within experimental error, with the exception of k_{OH}

for *p*-tolualdehyde obtained using *n*-butyl ether and benzaldehyde as reference compounds. To enable a direct comparison of the results obtained in this work with those reported by Thiault et al. [9], some of the same reference compounds (diethyl ether, *n*-hexane and benzaldehyde) were selected. For *o*-tolualdehyde, the average values obtained in this work and by Thiault et al. [9] are within 10% of each other and agree within experimental error. For *m*- and *p*-tolualdehyde, the average rate coefficients obtained in this work are 22% and 58% higher, respectively, than those reported by Thiault et al. [9]. For *p*-tolualdehyde, however, there is excellent agreement between the value obtained in this work and that measured by Volkamer et al. in the 200,000 L EUPHORE chamber [8], which was determined from a series of fourteen relative rate experiments using four different reference compounds. The fairly large discrepancy in the values obtained for *p*-tolualdehyde may be a result of difficulties in the handling and sampling of this compound due to its low volatility.

In an attempt to understand the reactivity of the aromatic aldehydes with OH radicals it is first appropriate to consider the reaction of the unsubstituted compounds, benzene and toluene. The reaction of OH radicals with aromatic compounds may proceed either by addition of OH to the aromatic ring or by H-atom abstraction. For ben-

Table 3
Reactant concentrations, slopes (k_1/k_2) and rate coefficients for the reaction of OH radicals with aromatic aldehydes at 295 ± 2 K

Aromatic	Concentration[a]	Reference	Concentration[a]	k_1/k_2[b]	k_{OH}[c]
Benzaldehyde	2.5–15	n-Butyl ether[d]	2.5–10	0.45 ± 0.04	12.96 ± 1.15
	3.8–7.5	Tetrahydrofuran[d]	3.8–7.5	0.80 ± 0.02	13.92 ± 0.35
	3.8–7.5	1,2,4-Trimethylbenzene[d]	3.8–7.5	0.45 ± 0.06	14.63 ± 1.95
	2.5–5.0	Diethyl ether[e]	2.5–5.0	1.05 ± 0.06	14.28 ± 0.82
	2.5–5.0	n-Hexane[e]	2.5–5.0	2.63 ± 0.12	14.20 ± 0.65
					14.0 ± 2.0[f]
o-Tolualdehyde	3.8–7.5	n-Butyl ether[d]	3.8–7.5	0.71 ± 0.04	20.45 ± 1.15
	3.8–7.5	1,2,4-Trimethylbenzene[d]	3.8–7.5	0.65 ± 0.04	21.13 ± 1.30
	2.5–6.8	Diethyl ether[e]	2.5–5.0	1.62 ± 0.06	22.03 ± 0.82
	2.5–6.8	n-Hexane[e]	2.5–6.8	3.55 ± 0.42	19.17 ± 2.27
	2.5–6.8	Benzaldehyde[e]	2.5–6.8	1.36 ± 0.12	19.31 ± 1.68
					20.4 ± 2.3[f]
m-Tolualdehyde	3.8–7.5	n-Butyl ether[d]	3.8–7.5	0.79 ± 0.04	22.75 ± 1.15
	3.8–7.5	Tetrahydrofuran[d]	3.8–7.5	1.24 ± 0.06	21.58 ± 1.04
	3.8–7.5	1,2,4-Trimethylbenzene[d]	3.8–7.5	0.64 ± 0.01	20.80 ± 0.33
	2.5–6.8	Diethyl ether[e]	2.5–5.0	1.46 ± 0.08	19.90 ± 1.09
	2.5–6.8	n-Hexane[e]	2.5–5.0	3.75 ± 0.44	20.25 ± 2.38
	2.5–6.8	Benzaldehyde[e]	2.5–5.0	1.36 ± 0.06	19.04 ± 0.84
					20.7 ± 2.4[f]
p-Tolualdehyde	3.8–7.5	n-Butyl ether[d]	3.8–7.5	0.77 ± 0.02	22.18 ± 0.58
	3.8–7.5	1,2,4-Trimethylbenzene[d]	3.8–7.5	0.67 ± 0.05	21.78 ± 1.63
	2.5–6.8	Diethyl ether[e]	2.5–6.8	1.38 ± 0.08	18.77 ± 1.09
	2.5–6.8	n-Hexane[e]	2.5–6.8	4.19 ± 0.40	22.63 ± 2.16
	2.5–6.8	Benzaldehyde[e]	2.5–6.8	1.24 ± 0.06	17.36 ± 0.84
					20.5 ± 2.2[f]

[a] Units of $\times 10^{14}$ molecule cm^{-3}.
[b] The indicated errors are twice the standard deviation arising from the least squares fit of the data.
[c] Units of $\times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.
[d] Experiment performed in the 350 L reaction chamber.
[e] Experiment performed in the 3910 L reaction chamber.
[f] Average value obtained in this work.

Table 4
Reactant concentrations, slopes (k_1/k_2) and rate coefficients for the reaction of NO$_3$ radicals with aromatic aldehydes at 295 ± 2 K

Aromatic	Concentration[a]	Reference	Concentration[a]	k_1/k_2[b]	k_{NO_3}[c]
Benzaldehyde	3.0–7.5	Tetrahydrofuran	3.0–11	0.85 ± 0.04	4.17 ± 0.20
	3.0–7.5	n-Propyl ether	2.0–5.0	0.92 ± 0.06	4.51 ± 0.29
					4.3 ± 0.3[d]
o-Tolualdehyde	3.0–5.8	Tetrahydrofuran	2.5–10	1.89 ± 0.06	9.26 ± 0.29
	3.0–5.8	n-Propyl ether	2.0–5.0	2.11 ± 0.08	10.34 ± 0.39
					9.8 ± 0.4[d]
m-Tolualdehyde	3.0–5.8	Tetrahydrofuran	2.5–10	1.91 ± 0.08	9.36 ± 0.39
	3.0–5.8	n-Propyl ether	2.0–5.0	1.95 ± 0.08	9.56 ± 0.39
					9.5 ± 0.4[d]
p-Tolualdehyde	3.0–5.8	Tetrahydrofuran	2.5–10	1.72 ± 0.14	8.43 ± 0.69
	3.0–5.8	n-Propyl ether	2.0–5.0	2.09 ± 0.08	10.24 ± 0.39
	3.0–5.8	Benzaldehyde	3.0–7.5	2.24 ± 0.16	9.72 ± 0.69
					9.5 ± 0.7[d]

[a] Units of $\times 10^{14}$ molecule cm^{-3}.
[b] The indicated errors are twice the standard deviation arising from the least squares fit of the data.
[c] Units of $\times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.
[d] Average value obtained in this work.

Table 5
Rate coefficients for the reaction of OH radicals with the aromatic aldehydes obtained in this study and previously reported literature values

Compound	k_{OH}[a]	T (K)	Reference compounds	Reference[a]
Benzaldehyde	14.0 ± 0.9	298 ± 2	Ethene-d$_4$	[5]
	11.8 ± 2.3	298 ± 4	Ethene	[6]
	13.0 ± 0.8	299	Diethyl ether	[7]
	12.5 ± 2.5	300 ± 8	1,3,5-Trimethylbenzene, phenol	[8]
	12.0 ± 2.0	298 ± 2	Diethyl ether, diisopropyl ether, 1,3-dioxolane	[9][b]
	14.0 ± 2.0	295 ± 2	n-Butyl ether, diethyl ether, 1,2,4-trimethylbenzene, n-hexane, tetrahydrofuran	This work[b]
o-Tolualdehyde	18.0 ± 2.0	298 ± 2	Diethyl ether, n-hexane, benzaldehyde, 1,3-dioxolane	[9][b]
	20.4 ± 2.3	295 ± 2	n-Butyl ether, diethyl ether, 1,2,4-trimethylbenzene, n-hexane, benzaldehyde	This work[b]
m-Tolualdehyde	17.0 ± 2.0	298 ± 2	Diethyl ether, n-hexane, benzaldehyde, 1,3-dioxolane	[9][b]
	20.7 ± 2.4	295 ± 2	n-Butyl ether, diethyl ether, 1,2,4-trimethylbenzene, n-hexane, benzaldehyde, tetrahydrofuran	This work[b]
p-Tolualdehyde	21.2	300 ± 8	Toluene, m-xylene, 1,3,5-trimethylbenzene, phenol	[8]
	13.0 ± 2.0	298 ± 2	Diethyl ether, n-hexane, benzaldehyde, 1,3-dioxolane	[9][b]
	20.5 ± 2.2	295 ± 2	n-Butyl ether, diethyl ether, 1,2,4-trimethylbenzene, n-hexane, benzaldehyde	This work[b]

[a] Units of $\times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.
[b] Average value.

zene OH addition is the predominant mechanism and a value of k_{OH}(benzene) = 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} is recommended in the evaluation by Calvert et al. [4]. Similarly for toluene, addition of OH to the aromatic ring dominates, with H atom abstraction from the methyl group accounting for only ∼6% of the reaction. The value of k_{OH}(toluene) = 5.6×10^{-12} cm^3 molecule^{-1} s^{-1} [4] is almost five times larger than the rate coefficient for benzene. The higher reactivity of toluene can be attributed to the presence of the methyl group which donates electron density to the aromatic ring inductively and activates the *ortho-* and *para-*positions towards addition of the electrophilic OH radical.

The rate coefficient for reaction of OH with benzaldehyde is one order of magnitude higher than that observed for benzene. Because the –CHO substituent is electron withdrawing, the aromatic ring in benzaldehyde is deactivated and addition of OH radicals is less favourable than in benzene. The large increase in reactivity observed for benzaldehyde over benzene may thus be attributed to the reaction of OH with the –CHO group, which proceeds mainly via abstraction of the aldehydic H-atom. In fact, the reactivity of benzaldehyde is very similar to that of acetaldehyde, k_{OH}(CH$_3$CHO) = 14.4×10^{-12} cm^3 molecule^{-1} s^{-1} [22], whose reactivity with OH is also dominated by H-atom abstraction from the –CHO group.

The rate coefficients obtained in this work show that, as expected, the tolualdehydes are more reactive than benzaldehyde due to the electron donating effect of the methyl substituent on the aromatic ring. In fact, the rate coefficients obtained for the tolualdehydes are approximately equal to the sum of the rate coefficients for toluene and benzaldehyde. Both H-atom abstraction (from the –CHO and CH$_3$ groups) and OH addition mechanisms are expected to occur and the relative contribution of these mechanistic pathways to the overall reactivity of the tolualdehydes can therefore be estimated. Based on the reactivity of benzaldehyde, the partial rate coefficient for H-atom abstraction from the –CHO group is approximately 14×10^{-12} cm^3 molecule^{-1} s^{-1}, which corresponds to ∼70% of the overall reactivity of the tolualdehydes. Based on the reac-

tivity of toluene, the partial rate coefficient for OH addition is approximately 5.5×10^{-12} cm^3 molecule^{-1} s^{-1}, which corresponds to ∼27% of the overall reactivity of the tolualdehydes. H-atom abstraction from the CH$_3$ group is a very minor channel, accounting for the remainder.

It is interesting to note that there is no difference in reactivity between the tolualdehyde isomers, which indicates that the relative positions of the –CHO and CH$_3$ groups have very little influence on the reactivity with OH. This is in stark contrast to compounds containing two electron donating substituents such as the xylenes and cresols. In these groups of compounds, the OH and CH$_3$ groups activate the *o-* and *p-*positions towards OH addition and the most reactive isomers are those with the largest number of unoccupied activated sites on the aromatic ring, i.e. *m*-xylene and *m*-cresol, see Table 6. The *o-* and *p*-isomers of the xylenes and cresols exhibit similar reactivity. For the tolualdehydes, the –CHO group is electron withdrawing at the *ortho-* and *para-*positions, whist the CH$_3$ group activates the *o-* and *p*-positions, as shown in Fig. 3. *m*-Tolualdehyde has the highest number of sites activated by the CH$_3$ group but these sites are also deactivated by the –CHO group. Similarly, *o-* and *p*-tolualdehyde contain equal numbers of activated and deactivated sites for OH addition. As a result *m*-tolualdehyde does not show any increase in reactivity over the two other isomers and it appears that for the tolualdehydes, the directing influence of the electron-donating CH$_3$ group is effectively cancelled out

Table 6
Recommended rate coefficients for the reaction of OH and NO$_3$ radicals with the xylenes and cresols [4]

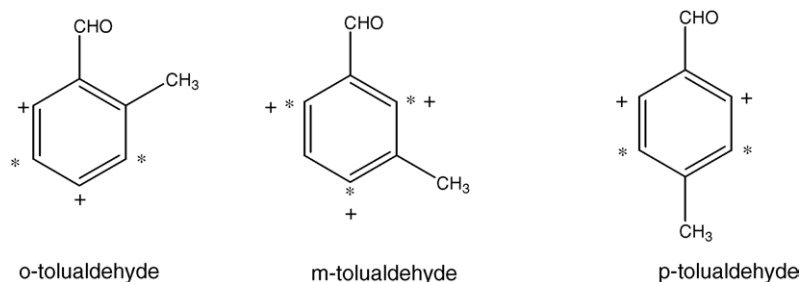| Compound	k_{OH}[a]	k_{NO_3}[a]
o-Xylene	14×10^{-12}	4.13×10^{-16}
m-Xylene	23×10^{-12}	2.60×10^{-16}
p-Xylene	14×10^{-12}	4.97×10^{-16}
o-Cresol	41×10^{-12}	1.40×10^{-11}
m-Cresol	68×10^{-12}	1.10×10^{-11}
p-Cresol	50×10^{-12}	1.10×10^{-11}

[a] Units of cm^3 molecule^{-1} s^{-1}.

Fig. 3. Diagram to show the effect of –CHO and –CH$_3$ groups on the reactivity of the aromatic aldehydes towards addition of OH radicals (asterisk (*) denotes sites activated towards OH addition, plus (+) denotes sites deactivated towards OH addition).

by the electron-withdrawing effect of the –CHO group and all of the tolualdehydes thus exhibit similar reactivity towards OH radicals. This argument is in contrast to that proposed by Thiault et al. [9], who, in an effort to explain their low value for k_{OH}(p-tolualdehyde), suggest that the activating effect of the methyl group in the tolualdehydes is less pronounced when located in the *para*-position. However, this statement is not consistent with the current understanding of the reactivity of aromatic compounds presented here. Consequently, we believe that the value of k_{OH}(p-tolualdehyde) determined by Thiault et al. [9] is too low and the rate coefficients obtained in this work and that of Volkamer et al. [8] are more in line with expectations.

4.2. NO$_3$ radical kinetics

The rates of reaction of NO$_3$ with benzaldehyde and the tolualdehydes at 295 ± 2 K were measured against two different reference compounds in the 350 L reaction chamber. The two relative rate coefficients obtained in this study for the reaction of NO$_3$ with benzaldehyde are in good agreement with each other and are within the range of the three previously reported rate coefficients, also obtained using the relative rate method: k_{NO_3}(benzaldehyde) = 2.4×10^{-15} to 8.0×10^{-15} cm^3 molecule^{-1} s^{-1} [10–12]. Given the scarcity of kinetic data on the reactions of NO$_3$ with aromatic compounds and suitable reference compounds, this represents a fairly good agreement. This is the first reported study of the reactions of NO$_3$ radicals with the tolualdehydes and a comparison with previous work is not possible. However, the rate coefficients obtained using the different reference compounds are in good agreement with each other.

The reactions of NO$_3$ radicals with aromatic compounds are generally much slower than the corresponding OH radical reactions. This is mainly because addition of NO$_3$ to the aromatic ring is not important and H-atom abstraction is therefore the dominant reaction mechanism [23]. Reaction of NO$_3$ with benzene is extremely slow with an upper limit of 3×10^{-17} cm^3 molecule^{-1} s^{-1} at 298 K [4], whilst reaction with toluene is only slightly faster, with k_{NO_3}(toluene) = 7.0×10^{-17} cm^3 molecule^{-1} s^{-1} (estimated overall uncertainty of a factor of 2), as recommended by Calvert et al. [4]. The rate coefficient for reaction of NO$_3$ with benzaldehyde is several orders of magnitude higher than that observed for benzene and toluene. This large increase in reactivity is due to H-atom abstraction from the –CHO group,

which is considerably more reactive than the CH$_3$ group in toluene.

As for the OH reaction, the rate coefficient for reaction of NO$_3$ radicals with benzaldehyde is very similar to that of acetaldehyde, k_{NO_3}(CH$_3$CHO) = 2.6×10^{-15} cm^3 molecule^{-1} s^{-1} [22] whose reactivity with NO$_3$ is also dominated by H-atom abstraction from the –CHO group.

The rate coefficients obtained in this study for the reaction of NO$_3$ with the tolualdehydes are just over two times greater than the value for benzaldehyde. Based on the low value for the rate coefficient for toluene, it seems unlikely that this increase in reactivity is due to H-atom abstraction from the CH$_3$ group. A more plausible explanation is that the reactivity of the –CHO group is affected by the presence of the methyl group on the aromatic ring. However, there appears to be no difference in reactivity between the tolualdehyde isomers, indicating that the relative positions of the –CHO and CH$_3$ groups have very little influence on the reactivity with NO$_3$. This is in stark contrast to compounds containing two electron donating substituents such as the xylenes and cresols, where the *meta* isomers exhibit lower reactivity than the *ortho* and *para* isomers, see Table 6. Although no reason for this observation is given in the literature [23], a possible explanation is that when the substituent groups are located in the *ortho*- or *para*-positions, they inductively donate electron density to each other thus making H-atom abstraction more facile. The *meta* isomers cannot benefit from this electron donating effect to the same extent and consequently have lower reactivity. The situation is clearly different for the tolualdehydes, which contain an electron-withdrawing –CHO group and an electron-donating CH$_3$ group. The fact that *m*-tolualdehyde does not show any decrease in reactivity compared to the two other isomers indicates that the directing influence of the electron-donating CH$_3$ group is effectively cancelled out by the electron-withdrawing effect of the –CHO group and all of the tolualdehydes thus exhibit similar reactivity towards NO$_3$ radicals.

In contrast to the OH reactions, the rate coefficients for reaction of NO$_3$ radicals with the tolualdehydes are *not* approximately equal to the sum of the rate coefficients for toluene and benzaldehyde. This difference is due to the fact that the reactions of OH and NO$_3$ radicals with toluene predominantly occur *via* different mechanisms; addition and H-atom abstraction, respectively. The partial rate coefficients for the reactions of OH and NO$_3$ radicals with the 'toluene part' of the tolualdehydes account for about 30% and 0.7% of the overall reactivity,

respectively. Nevertheless, because H-atom abstraction from the –CHO group is the dominant reaction pathway for both OH and NO$_3$ reactions, a correlation between the rate coefficients may be expected.

4.3. Correlation of the OH and NO$_3$ radical rate coefficients

Nielsen and co-workers [22] have shown that a good correlation exists between the OH and NO$_3$ radical rate coefficients for the aliphatic aldehydes. The data obtained in this work can be used to determine whether a similar correlation exists for the aromatic aldehydes. The general form of these correlations is a linear relationship between the logarithms of the rate coefficients for the reaction of NO$_3$ and those for the reaction of OH with a particular series of substrates [23].

$$\log(k_{NO_3}) = m \times \log(k_{OH}) + c \quad (III)$$

The basis for these empirical correlations can be found in the thermodynamic expression of transition-state theory, according to which a rate coefficient, k, can be expressed in terms of a free energy of activation, ΔG,

$$k = \left(\frac{k_B T}{h}\right) \exp\left(-\frac{\Delta G}{RT}\right) \quad (IV)$$

where k_B is the Boltzmann constant and h is Plank's constant. Combining Eqs. (III) and (IV) yields a so-called linear free energy relationship, which can be used to identify patterns of chemical reactivity.

Following Wayne et al. [23], a series of 58 compounds have been selected and correlation lines for abstraction and addition

reactions have been drawn based on recent evaluations of the rate coefficients for reaction with OH and NO$_3$ radicals at 298 K [4,24–26]. The 20 compounds used to construct the correlation line for abstraction reactions include alkanes, formaldehyde, acrolein, methylene chloride and aromatics.

For H-atom abstraction from saturated hydrocarbons, the correlation is given by:

$$\log(k_{NO_3}) = (0.87 \pm 0.12) \times \log(k_{OH}) + (-6.0 \pm 1.3)$$

with $r = 0.94$.

The 38 compounds used to construct the correlation line for addition reactions include alkenes, alkynes, cycloalkenes, terpenes, styrene, acenaphthylene, ethyl mercaptan, pyrrole, chloroethene and 1,1-dichloroethene. For addition to unsaturated hydrocarbons, the correlation is given by:

$$\log(k_{NO_3}) = (3.42 \pm 0.30) \times \log(k_{OH}) + (22.7 \pm 3.2)$$

with $r = 0.94$.

The correlation lines for abstraction and addition reactions are shown in Fig. 4 along with the data points for the 4 aromatic aldehydes studied in this work and those obtained by D'Anna et al. for 15 (C$_2$–C$_6$) aliphatic aldehydes [22]. Clearly the aromatic and aliphatic aldehydes fall close to the correlation line for addition reactions and not close to the line for abstraction reactions. It is also noted that the aldehydes react with the NO$_3$ radical close to an order of magnitude faster than the predicted value calculated by H-atom abstraction correlation. This implies that the reactions of OH and NO$_3$ radicals with aliphatic and aromatic aldehydes are not just straightforward H-atom abstraction reactions. As discussed by D'Anna et al. [22], the available experimental and theoretical evidence suggests that the reac-

Fig. 4. Linear free energy plot for the reactions of OH and NO$_3$ radicals with a series of 15 aliphatic and 4 aromatic aldehydes. Also shown are the correlation lines for H-atom abstraction and addition reactions.
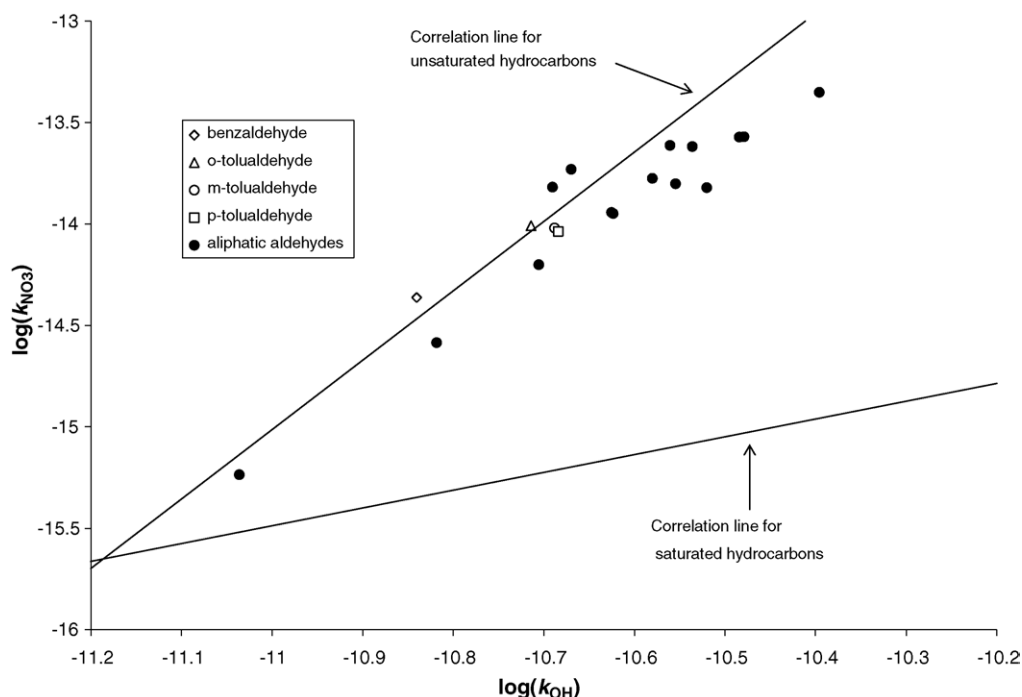
Table 7
Net atomic charges calculated for the carbon atoms in the ring, where carbon no. 1 is always the carbon bonded to the –CHO group (In addition, the net atomic charge on the hydrogen atom in the –CHO group is presented.)

Atom	Benzene	Toluene	Benzaldehyde	o-Tolualdehyde	m-Tolualdehyde	p-Tolualdehyde
Ring carbon 1	−0.1021	−0.0744	−0.2013	−0.1977	−0.1956	−0.2092
Ring carbon 2	−0.1021	−0.1055	−0.0557	−0.0205	−0.0597	−0.0501
Ring carbon 3	−0.1021	−0.0971	−0.1190	−0.1286	−0.0904	−0.1238
Ring carbon 4	−0.1021	−0.1089	−0.0698	−0.0642	−0.0714	−0.0407
Ring carbon 5	−0.1021	−0.0980	−0.1195	−0.1265	−0.1150	−0.1219
Ring carbon 6	−0.1021	−0.1030	−0.0339	−0.0342	−0.0412	−0.0284
H atom in –CHO group			0.0450	0.0525	0.0445	0.0442

tions are not simple bimolecular elementary reactions and that the apparent addition reaction behaviour is due to the formation of a pre-reaction adduct between the radical and –CHO part of the aldehyde molecule. The adduct can undergo C−H bond cleavage with the overall reaction being equivalent to H-atom abstraction by the attacking radical species.

4.4. Theoretical calculations

Some theoretical calculations have been performed at the PM3 level for o-, m- and p-tolualdehyde, benzaldehyde and toluene, to determine the relative importance of the inductive effects of the methyl group versus the electron withdrawing nature of the –CHO group for the tolualdehydes. The results of the calculations are shown in Table 7. The calculations show that the partial charge on the aldehydic hydrogen becomes more positive on going from p-tolualdehyde and m-tolualdehyde to o-tolualdehyde. Therefore if abstraction of the aldehydic proton is the dominant mechanism, one would expect that the rate coefficients would be very similar for p-tolualdehyde and m-tolualdehyde and slightly larger for o-tolualdehyde, reflecting the change in net atomic charge. This is indeed the case for reaction with Cl atoms [9] and NO$_3$ radicals, where abstraction is believed to be the dominant mechanism. For the NO$_3$ reactions, however, a certain amount of reservation must be retained because although the rate coefficients follow the expected pattern, they are in fact equal within experimental error.

For the reaction of OH radicals with the tolualdehydes, the trend is different, with the rate coefficients for all three isomers being the same within experimental error. Inspection of the net atomic charges at the carbon atoms within the ring and their comparison with benzaldehyde reveals a possible explanation. As shown in Fig. 3, o- and p-tolualdehyde each have two sites which are activated (inductive effect) with respect to OH addition to the ring, whilst m-tolualdehyde potentially has three sites depending on whether the inductive or electron withdrawing effects dominate. For m-tolualdehyde, it emerges that all three sites are activated when compared with benzaldehyde, i.e. inductive effects dominate. For p-tolualdehyde, the two sites labeled are activated but the carbon bonded to the –CHO group is also activated, i.e. three sites. However, for o-tolualdehyde, the two sites labeled are indeed activated but the carbon bonded to the –CHO group shows virtually no change in activation compared with benzaldehyde. If addition of OH to the ring were occur-

ring it would be envisaged that the order of reactivity would be o-tolualdehyde < p-tolualdehyde ~ m-tolualdehyde. Thus o-tolualdehyde is expected to be the least reactive isomer with respect to OH addition but the most reactive isomer with respect to H-atom abstraction from the aldehyde group. For the tolualdehydes, the combination of the inductive effects of the methyl group and the electron withdrawing nature of the –CHO group results in all isomers bearing the same reactivity towards OH radicals. Theoretical calculations at this level can only be used qualitatively, but they are consistent with both abstraction (major) and addition (minor) mechanisms taking place in the reaction of OH with the tolualdehydes and that the slight change in order of reactivity for OH and the tolualdehydes compared with NO$_3$, is because addition to the ring is significant.

4.5. Atmospheric implications

The possible atmospheric loss processes for the aromatic aldehydes are photolysis by solar radiation and gas-phase reaction with OH, NO$_3$, Cl and O$_3$. Uptake by water droplets is also possible, but since the main component of the molecules are aromatic and thus hydrophobic, this process is unlikely to be of any importance. The reaction with ozone has not been studied before, but is expected to be very slow and also of negligible importance [1]. Reaction with Cl is only important in marine environments where there are significantly high concentrations of Cl atoms [9] and preliminary results on the photolysis of the aromatic aldehydes, indicate that this process is only important for o-tolualdehyde [27].

The rate coefficients determined in this work for the reaction of OH and NO$_3$ radicals with the aromatic aldehydes can be used to calculate the lifetimes of the compounds in the troposphere. The tropospheric lifetime of a compound with respect to reaction with a species X can be calculated by: lifetime $(\tau_x) = 1/k_x[X]$, where k_x is the bimolecular rate coefficient and [X] is the tropospheric concentration of the reactive species. The tropospheric lifetimes due to reaction with OH and NO$_3$ have been calculated using 12 h daily average values of [OH] = 1.6×10^6 molecule cm^{-3} [1] and [NO$_3$] = 5×10^8 molecule cm^{-3} [28] and are listed in Table 8. The tropospheric lifetimes due to photolysis, $\tau_p = 1/k_p$, [27] and reaction with Cl [9] are also provided for comparative purposes.

The calculated tropospheric lifetimes listed in Table 8 show that reaction with OH radicals is the most important atmospheric

Table 8
Atmospheric lifetimes for the reaction of OH, NO$_3$ and Cl with benzaldehyde, *o*-, *m*- and *p*-tolualdehyde

Compound	τ_{OH} (h)	k_{NO_3} (h)	τ_p (h)	τ_{Cl} (months)
Benzaldehyde	19.8	128.0	>144	4
o-Tolualdehyde	13.6	56.7	2.5	2
m–Tolualdehyde	13.4	58.7	>144	2.3
p-Tolualdehyde	13.5	58.7	>144	2.7

degradation pathway for all of the aromatic aldehydes except *o*-tolualdehyde, which mainly undergoes photolysis. The relatively short lifetimes for the aromatic aldehydes indicate that, if released or formed in the atmosphere, they will undergo degradation in the troposphere and contribute to regional ozone formation. The fate of the oxidation products will also be important as further atmospheric degradation of these compounds can also contribute to the formation of ozone and other oxidants. Furthermore, the high branching ratios for the H-atom abstraction pathway in the aromatic aldehydes suggests high yields of aromatic nitrate compounds (peroxybenzylnitrates) are likely to be formed, which are reservoirs of NO$_x$.

Acknowledgements

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