

Rate Coefficients for the Gas-Phase Reaction of Hydroxyl Radicals with the Dimethylbenzaldehydes

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ABSTRACT: Rate coefficients for the reactions of hydroxyl (OH) radicals with the dimethylbenzaldehydes have been determined at $295 \pm 2\text{K}$ and atmospheric pressure using the relative rate technique. Experiments were performed in an atmospheric simulation chamber using gas chromatography for chemical analysis. The rate coefficients (in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) are: 2,3-dimethylbenzaldehyde, $(25.9 \pm 2.8) \times 10^{-12}$; 2,4-dimethylbenzaldehyde, $(27.5 \pm 4.4) \times 10^{-12}$; 2,5-dimethylbenzaldehyde, $(27.6 \pm 5.1) \times 10^{-12}$; 2,6-dimethylbenzaldehyde, $(30.7 \pm 3.0) \times 10^{-12}$; 3,4-dimethylbenzaldehyde, $(24.6 \pm 4.0) \times 10^{-12}$; and 3,5-dimethylbenzaldehyde, $(28.2 \pm 2.5) \times 10^{-12}$. The reactivity of the dimethylbenzaldehydes is compared with other aromatic compounds and it is shown that the magnitude of the OH rate coefficients does not depend significantly on the position of the CH_3 substituent on the aromatic ring. The rate coefficient data are explained in terms of known mechanistic features of the reactions and the atmospheric implications are also discussed. © 2006 Wiley Periodicals, Inc. *Int J Chem Kinet* 38: 563–569, 2006

INTRODUCTION

Dimethylbenzaldehydes (DMBAs) are released into the atmosphere from automobile emissions [1] and wood smoke [2]. They can also be formed in the atmosphere through degradation of the trimethylbenzene isomers; e.g., 2,4-, 2,5- and 3,4-dimethylbenzaldehyde are all produced from the hydroxyl (OH) radical initiated oxidation of 1,2,4-trimethylbenzene [3,4]. The DMBAs 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 troposphere. In order to fully understand the environmental impact of the dimethylbenzaldehydes, a detailed knowledge of the kinetics and mechanisms for their atmospheric degradation is required.

The major atmospheric loss processes for the DMBAs are expected to be gas-phase reaction with OH and NO_3 radicals and photolysis by sunlight [5]. Very little information exists in the literature on the reactivity of dimethylbenzaldehydes. Tse et al. [6] measured rate coefficients for the reaction of OH radicals with 2,4-, 2,5- and 3,4-dimethylbenzaldehyde using the relative rate technique. Volkamer et al. [7] determined the rate coefficient for the reaction of 3,5-dimethylbenzaldehyde

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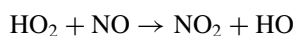
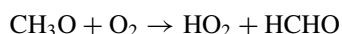
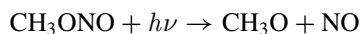
with OH radicals, also using the relative rate method. The reported values of k_{OH} for the four different DMBA isomers vary considerably, which is somewhat surprising, given that the three isomers of tolualdehyde exhibit very similar reactivity towards OH radicals [8,9].

In this study, rate coefficients have been determined for the reaction of hydroxyl radicals with the six isomers of dimethylbenzaldehyde. The reactivity of the DMBA isomers is compared to other aromatic compounds and the rate coefficients are also used to calculate atmospheric lifetimes for reaction with OH radicals.

EXPERIMENTAL

Rate coefficients for the reactions of the DMBA isomers with OH radicals at $295 \pm 2\text{ K}$ 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 an atmospheric simulation chamber filled to atmospheric pressure with purified air and equipped with gas chromatography for chemical analysis. The chamber, which has been described in detail elsewhere [9,10], is a cylinder consisting of an FEP Teflon foil tube (4.1 m long, 1.1 m diameter) closed at both ends by aluminum plates covered with FEP foil. At atmospheric pressure, the chamber has a volume of 3.91 m^3 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 DMBA isomers 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. The photolysis of methyl nitrite was used as the OH radical source:



Measured amounts of methyl nitrite were flushed from a Pyrex bulb into the chamber by a stream of purified air. A gas chromatograph 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: $[\text{CH}_3\text{ONO}] = (1.2\text{--}2.0) \times 10^{15}$, $[\text{DMBA}] = (1.8\text{--}3.7) \times 10^{14}$, and $[\text{reference}] = (1.8\text{--}3.7) \times 10^{14}$. In all experiments, the initial

concentration of substrate and reference compounds was 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 reactant mixtures were photolyzed for 1–2 min and a gas chromatograph of the chamber contents was taken. In the experiments performed on the DMBA isomers, nine of the TL05 lamps were used, corresponding to an estimated value of $J(\text{NO}_2) = 8 \times 10^{-4}\text{ s}^{-1}$ in the chamber. The photolysis-sampling procedure was repeated until around 30% depletion of the substrate and reference compound was achieved. Typically, four to seven photolysis-sampling steps were carried out during each experiment. Experiments were performed on the DMBA isomers separately using two or three reference compounds. At least two (and in most cases three) runs were carried out with each DMBA–reference combination.

Before kinetic experiments were carried out, the possibility of wall loss and photolysis of the dimethylbenzaldehydes was 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.

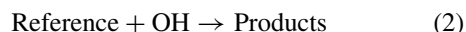
A high-performance gas chromatograph equipped with a flame ionization detector (Varian CP3800, Varian Inc., Palo Alto, CA), directly connected to the reaction chamber via a six port gas sampling valve (Valco Instruments, Houston, TX), was used for chemical analysis. The valve is fitted with a 1 cm^3 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 Inc., 30 m, 0.53 mm i.d., 0.5 μm film thickness). The column was operated using a flow rate of $5\text{ cm}^3\text{ min}^{-1}$ and an initial oven temperature of 90°C , which was then increased to 170°C at a rate of $10^\circ\text{C min}^{-1}$ after elution of the reference compound. Chromatographs were recorded and analyzed using the Varian software. The relative concentrations of each compound were determined from peak area measurements during analyses.

The compounds used in this study, their manufacturer, and stated purity were as follows:

2,3-dimethylbenzaldehyde (Aldrich, 97%), 2,4-dimethylbenzaldehyde (Aldrich, 97%), 2,5-dimethylbenzaldehyde (Aldrich, 99%), 2,6-dimethylbenzaldehyde (Aldrich, 97%), 3,4-dimethylbenzaldehyde (Aldrich, 98%), 3,5-dimethylbenzaldehyde (Aldrich, 97%), *n*-propyl ether (Aldrich, 99+%), *n*-butyl ether (Aldrich, 99.5%), and 1,2,4-trimethylbenzene (Aldrich, 98%). Methyl nitrite was synthesized following the method of Taylor et al. [11] and its purity was checked by an FTIR spectroscopy.

RESULTS

Rate coefficients for the reactions of the DMBA isomers with OH were determined by comparing the rates of decay of the reactant relative to that of selected reference compounds:



Because of their low volatility, the DMBA isomers were also lost to the walls of the reactor via deposition:



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

$$\ln \frac{[\text{DMBA}]_0}{[\text{DMBA}]_t} - k_{\text{wall}}t = \frac{k_1}{k_2} \ln \frac{[\text{reference}]_0}{[\text{reference}]_t} \quad (I)$$

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 2,3-, 2,4-, 2,5-, and 2,6-DMBA isomers, however, were found to be susceptible to photolysis by the lamps used to generate OH radicals.



No photolysis was observed for 3,4- and 3,5-DMBA or any of the reference compounds. Incorporating photolysis into Eq. (I) yields the following relationship:

$$\ln \frac{[\text{DMBA}]_0}{[\text{DMBA}]_t} - k_{\text{wall}}t - k_p t_p = \frac{k_1}{k_2} \ln \frac{[\text{reference}]_0}{[\text{reference}]_t} \quad (II)$$

where k_p is the rate coefficient representing the photolysis of the DMBA isomer. It should be noted that wall loss was occurring throughout the experiment while 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 3,4- and 3,5-DMBA, plots in the form of Eq. (I) should yield a straight line with zero intercept and slope k_1/k_2 . For 2,3-, 2,4-, 2,5-, and 2,6-DMBA, plots in the form of Eq. (II) are appropriate.

The photolysis and wall loss rates were determined for each of the DMBA isomers and are summarized in Table I. Significant photolysis rates were observed for 2,3-, 2,4-, 2,5-, and 2,6-DMBA. For these isomers, photolysis accounted for up to 30% of their overall decay. Wall loss accounted for 0.4–12% of the overall decay of the DMBA isomers. The importance of correcting for photolysis and wall loss is clearly apparent.

The rate of reaction of each DMBA isomer was compared to that of two or three reference compounds. The reference compounds used in this study and their rate coefficients for reaction with OH (k_2 , in units of $\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) were as follows: *n*-butyl ether (28.9 ± 2.3), *n*-propyl ether (19.9 ± 1.7), and 1,2,4-trimethylbenzene (32.5 ± 4.8). The reference rate coefficients used for *n*-butyl ether [12] and 1,2,4-trimethylbenzene [13] are the values most recently reported in the literature. For *n*-propyl ether, several values have been reported [14–16] and it was decided to choose the value of Nelson et al. [16] as both the absolute and relative rate studies are in excellent agreement. Plots in the form of Eq. (II) for 2,3-, 2,4-, 2,5-, and 2,6-DMBA and Eq. (I) for 3,4- and 3,5-DMBA are linear with near-zero intercepts as shown in Fig. 1. A summary of the slopes derived from the plots and calculated OH rate coefficients is provided in Table II. The indicated errors on k_1 are twice the standard deviation arising from the least squares fit of the data and include the reported errors in the reference rate coefficients, k_2 .

Table I Photolysis and Wall Loss Rates for the Dimethylbenzaldehyde Isomers

Compound	Photolysis Loss (s^{-1}) ^a	Wall Loss (s^{-1}) ^a
2,3-DMBA	$(1.8 \pm 0.4) \times 10^{-5}$	$(1.4 \pm 0.8) \times 10^{-6}$
2,4-DMBA	$(2.0 \pm 0.5) \times 10^{-5}$	$(1.6 \pm 0.8) \times 10^{-6}$
2,5-DMBA	$(2.0 \pm 0.6) \times 10^{-5}$	$(2.8 \pm 0.7) \times 10^{-7}$
2,6-DMBA	$(1.7 \pm 0.2) \times 10^{-5}$	$(3.3 \pm 0.9) \times 10^{-6}$
3,4-DMBA	—	$(4.3 \pm 1.0) \times 10^{-6}$
3,5-DMBA	—	$(9.0 \pm 1.9) \times 10^{-6}$

^a Errors are twice the standard deviation arising from the least squares fit of the data.

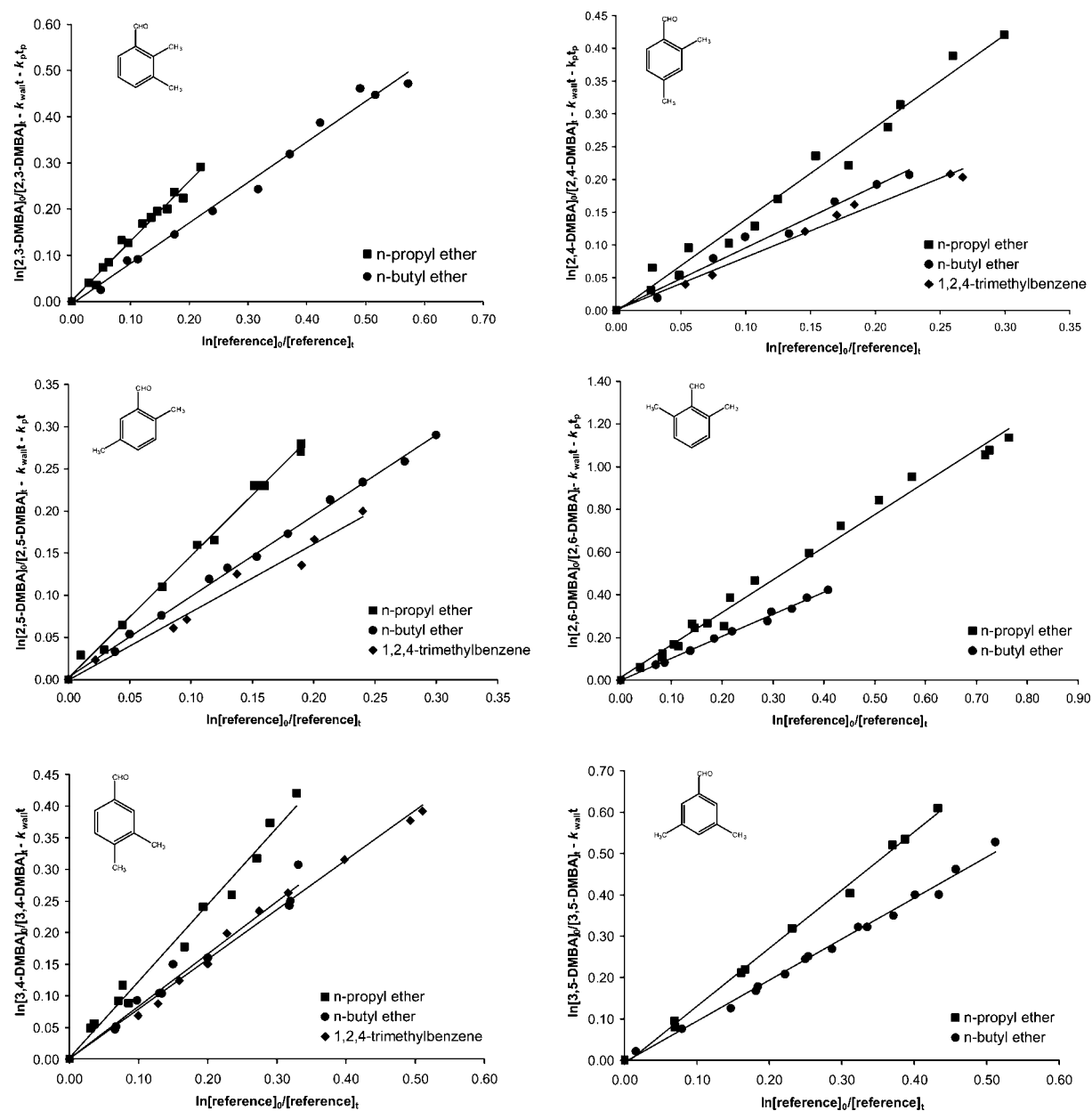


Figure 1 Relative rate plots for the reaction of OH radicals with the six dimethylbenzaldehyde isomers at $295 \pm 2\text{K}$.

DISCUSSION

Comparison with Literature Data

The rates of reaction of OH radicals with the dimethylbenzaldehydes at $295 \pm 2\text{K}$ were measured against at least two different reference compounds. As shown in Table II, the rate coefficients determined in this work using the different reference compounds are in excellent agreement. The average values of the rate coefficients are compared with the available literature data in Table III.

The data obtained for 3,4- and 3,5-DMBA in this work are in reasonable agreement with the previously reported values. However, the rate coefficients for 2,4- and 2,5-DMBA reported by Tse et al. [6] are about 60% higher than those obtained in this study. The most likely reason for this discrepancy is that Tse et al. [6] did not take into account other possible losses for 2,4- and 2,5-DMBA in their reactor system such as photolysis or wall loss. Tse et al. performed their experiments under very similar conditions to those employed in this work—they also used a Teflon reactor (1 m^3) and “black lamps” to generate OH radicals—but did

Table II Rate Coefficients for the Reaction of OH with the Dimethylbenzaldehydes Obtained in This Work

Compound	Reference	k_1/k_2^a	k_{OH}^b
2,3-DMBA	<i>n</i> -Butyl ether	0.89 ± 0.05	25.72 ± 2.51
	<i>n</i> -Propyl ether	1.31 ± 0.08	26.07 ± 2.74
			25.9 ± 2.8^c
2,4-DMBA	<i>n</i> -Butyl ether	0.96 ± 0.10	27.74 ± 3.64
	<i>n</i> -Propyl ether	1.41 ± 0.10	28.06 ± 3.12
	1,2,4-Trimethylbenzene	0.82 ± 0.06	26.65 ± 4.39
			27.5 ± 4.4^c
2,5-DMBA	<i>n</i> -Butyl ether	0.96 ± 0.03	27.74 ± 2.37
	<i>n</i> -Propyl ether	1.45 ± 0.06	28.86 ± 2.74
	1,2,4-Trimethylbenzene	0.81 ± 0.10	26.33 ± 5.07
			27.6 ± 5.1^c
2,6-DMBA	<i>n</i> -Butyl ether	1.06 ± 0.04	30.63 ± 2.70
	<i>n</i> -Propyl ether	1.55 ± 0.07	30.85 ± 2.98
			30.7 ± 3.0^c
3,4-DMBA	<i>n</i> -Butyl ether	0.83 ± 0.08	23.99 ± 3.00
	<i>n</i> -Propyl ether	1.21 ± 0.08	24.08 ± 2.60
	1,2,4-Trimethylbenzene	0.79 ± 0.04	25.68 ± 4.01
			24.6 ± 4.0^c
3,5-DMBA	<i>n</i> -Butyl ether	0.99 ± 0.02	28.61 ± 2.35
	<i>n</i> -Propyl ether	1.40 ± 0.04	27.86 ± 2.51
			28.2 ± 2.5^c

^a The indicated errors are twice the standard deviation arising from the least squares fit of the data.^b In units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.^c Average value obtained in this work.

not measure wall loss and reported “no significant loss due to photolysis” [6]. This latter finding is somewhat surprising, given that photolysis was responsible for up to 30% of the decay of 2,3-, 2,4-, 2,5-, and 2,6-DMBA in this work, and that photolysis by sunlight has recently been found to be a significant atmospheric loss process for these isomers [19,20]. In the present study, it was necessary to correct the measured losses of the compounds for photolysis and wall loss in order to obtain an accurate value for the rate coefficients. It

is interesting to note that the rate coefficients obtained by Tse et al. [6] for 3,4-DMBA and by Volkamer et al. [7] for 3,5-DMBA are in reasonable agreement with the values obtained in this work. These two isomers are not photolyzed by the “black lamps” or sunlight and hence no correction due to photolysis is required. This study represents the first determination of the rate coefficients for the reaction of OH radicals with 2,6- and 2,3-DMBA and therefore a comparison with the literature is not possible.

Table III Rate Coefficients for the Reaction of OH Radicals with the Dimethylbenzaldehydes Obtained in This Study and Previously Reported Literature Data

Compound	k_{OH}^a	T (K)	Technique ^b	Reference
2,3-DMBA	25.9 ± 2.8	295 ± 2	RR	This work
2,4-DMBA	43.2 ± 6.7	298 ± 2	RR	[6]
	27.5 ± 4.4	295 ± 2	RR	This work
2,5-DMBA	43.7 ± 6.8	298 ± 2	RR	[6]
	27.6 ± 5.1	295 ± 2	RR	This work
2,6-DMBA	30.7 ± 3.0	295 ± 2	RR	This work
3,4-DMBA	21.4 ± 3.4	298 ± 2	RR	[6]
	24.6 ± 4.0	295 ± 2	RR	This work
3,5-DMBA	34.0 ± 6.8	300 ± 8	RR	[7]
	28.2 ± 2.5	295 ± 2	RR	This work

^a In units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.^b RR: relative rate.

Trends in Reactivity

The rate coefficients obtained in this study for the reaction of OH with the dimethylbenzaldehydes are higher than those determined for the tolualdehydes, which, in turn, are higher than the rate coefficient for benzaldehyde. The observed increase in reactivity of the aromatic aldehydes with the increasing degree of substitution is largely due to the inductive electron-donating effect of the CH_3 groups, which results in the activation of the *ortho* and *para* positions towards addition of the electrophilic OH radical. The predominant mechanism for the reaction of OH radicals with benzaldehyde ($k_{OH} = 14 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is H-atom abstraction from the $-\text{CHO}$ group [4]. Addition of a CH_3 group to form the

tolualdehydes causes the rate coefficient to increase to about $20 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [9]. The rate coefficients for the tolualdehydes are approximately equal to the sum of the rate coefficients for the reaction of OH with benzaldehyde and toluene ($k_{\text{OH}} = 5.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [4]). This implies that the $-\text{CHO}$ and CH_3 groups contribute about 70% and 30% to the overall reactivity of the tolualdehydes, respectively. The addition of a further CH_3 group to form the dimethylbenzaldehydes causes the rate coefficient to increase to about $27 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (average for all six isomers). The rate coefficients for the dimethylbenzaldehydes are approximately equal to the sum of the rate coefficients for the reaction of OH with the tolualdehydes and toluene. This implies that the $-\text{CHO}$ and CH_3 groups each contribute about 50% to the overall reactivity of the dimethylbenzaldehydes.

The rate coefficient data obtained in this work can also be compared to the values calculated using the structure-activity relationship (SAR) developed by Kwok and Atkinson [17]. The approach uses experimentally derived data to assign a partial rate coefficient to each reactive site in the molecule and is utilized in the AOP WIN rate coefficient calculator operated by the US Environmental Protection Agency [18]. The calculated rate coefficients (in units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reaction of OH with the DMBAs are as follows: 2,3-, 2,5- and 3,4-DMBA (20.3); 2,4- and 2,6-DMBA (21.5), and 3,5-DMBA (23.9). For all isomers, H-atom abstraction from the aldehyde group is assigned a partial rate coefficient of $17.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with the remaining reactivity attributed to OH addition. However, since the calculated rate coefficients are 15–30% lower than the experimental values obtained in this work, then it seems likely that the SAR method may underestimate the contribution of OH addition in these reactions.

The effect of the CH_3 groups in the tolualdehydes and dimethylbenzaldehydes is to activate the aromatic ring to addition of OH radicals. For the tolualdehydes, there is no difference in reactivity between the isomers, which indicates that the relative positions of the CH_3 groups have very little influence on the reactivity with OH radicals. For the dimethylbenzaldehydes, although there are small differences in the measured rate coefficients, there is no significant difference in reactivity between the isomers, which indicates that the presence of an additional CH_3 group is not sufficient to give rise to a noticeable directing effect. This observation is in stark contrast to compounds containing only electron-donating substituents such as the trimethylbenzenes and dimethylphenols. In these groups of compounds,

the OH and CH_3 groups activate the *ortho* and *para* positions towards OH addition and the most reactive isomers are those with the largest number of activated sites on the aromatic ring, i.e., 1,3,5-trimethylbenzene and 3,5-dimethylphenol, [4]. The other trimethylbenzene isomers contain the same number of activated sites and therefore exhibit similar reactivity, while for the dimethylphenols, the 2,4- and 2,6-isomers contain the lowest number of unoccupied activated sites and are the least reactive. For the dimethylbenzaldehydes, the $-\text{CHO}$ group is electron withdrawing at the *ortho* and *para* positions, while the CH_3 group activates the *ortho* and *para* positions. 3,5-DMBA has the highest number of sites activated by the CH_3 group, but these sites are also deactivated by the $-\text{CHO}$ group. As a result, 3,5-DMBA does not show any significant increase in reactivity over the other isomers and it appears that for the dimethylbenzaldehydes, the directing influence of the electron-donating CH_3 group is effectively cancelled out by the electron-withdrawing effect of the $-\text{CHO}$ group and all of the isomers thus exhibit similar reactivity towards OH radicals.

Atmospheric Implications

The rate coefficients determined in this work can be used to calculate the atmospheric lifetimes of the dimethylbenzaldehydes with respect to reaction with OH. The atmospheric lifetime (τ) is defined as the time taken for the concentration of a species to decrease to $1/e$ of its initial value. Using the formula lifetime (τ) = $1/k_{\text{OH}}[\text{OH}]$, and assuming a 12 h daily average value of $[\text{OH}] = 1.6 \times 10^6 \text{ molecule cm}^{-3}$ [5], lifetimes in the range 5.6–7.1 h are calculated for the dimethylbenzaldehydes. These relatively short lifetimes indicate that, if released or formed in the atmosphere, the DMBAs will rapidly undergo degradation in the troposphere and may have an impact on local air quality. As a consequence, the fate of the OH initiated oxidation products will also be of importance as further atmospheric degradation of these compounds can also contribute to the formation of ozone and other oxidants. Reaction of aromatic aldehydes with OH in the presence of NO_x is known to produce peroxybenzyl nitrates and nitro-aromatic compounds [4].

In order to further our knowledge of the competing atmospheric degradation pathways for the DMBAs, kinetic data is required for their photolysis by sunlight and reaction with NO_3 radicals. Unfortunately, there is no experimental data available for the reactions of NO_3 with the DMBAs and the SAR estimation method does not include these reactions [17]. However, if it is assumed that the dimethylbenzaldehydes exhibit a similar level of reactivity as the tolualdehydes, then the

reaction with NO_3 radicals is expected to be a minor loss process for the DMBA isomers [9]. Investigations into the atmospheric photolysis of the DMBA isomers have recently been performed [19] and indicate that photolysis by sunlight is an important atmospheric loss process for 2,3-, 2,4-, 2,5-, and 2,6-DMBA, with estimated photolysis lifetimes in the range 1–10 h. Details concerning the photolysis of the DMBA isomers are the subject of a forthcoming publication [20].

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