

Authors' response to all referees for ACP-2020-281

The authors would like to thank all the referees for their overall very positive support for this work and their helpful and insightful comments. Below is a breakdown of all referee comments (*black italics*) with appropriate author responses (*blue text*).

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Anonymous Referee #1

The paper "Rate coefficients for reactions of OH with aromatic and aliphatic volatile organic compounds determined by the Multivariate Relative Rate Technique" by J. Shaw et al. describes the application of a recently developed technique for the measurement of relative rate coefficients of complex mixtures. The technique had been already presented in an earlier work by the same authors, but has been improved in this work to allow also the measurement of rate constants for slower reacting hydrocarbons. The technique has been validated by the measurement of well-known rate constants, and the overall measurements are used to validate SAR models. The rate constants of 5 species have also been measured for the first time. The work is well done and within the scope of ACP. I recommend publication after considering the following minor remarks.

15 The authors would like to thank the referee for their supportive review.

Introduction: page 3, line 13, please precise at first use what C_x substituted aromatics means.

C_x refers to the number of carbon atoms in the substituent groups attached to the benzene ring of an aromatic molecule. We acknowledge that the first use of this terminology on page 3 could be better clarified, therefore we have changed the text to read "monoaromatics containing four carbons as part of alkyl substituents (henceforth C₄ aromatics)" and later further clarified on line 27 "Monoaromatics with two or three alkyl substituents, each containing one, two or three carbons (henceforth C₁, C₂ or C₃ substituents) have relatively large POCP values meaning that they are amongst the emitted species with the greatest potential for producing ozone (Derwent et al., 2007)."

Page 4, line 9: change "." to ","

25 We are unsure which punctuation is referred to here. The only full stop (period) in Page 4, Line 9 comes at the end of a sentence which is not linked to the following sentence. We would welcome any advice / clarification from the reviewer or the editorial team on this point.

Page 6: how can you be sure that all H is converted into rather unreactive HO₂? Is there a possibility that H- atoms survive into the reaction zone and react more or less fast with the different VOCs?

30 Atomic H will react particularly fast with O₂ under these conditions. Reaction R2 (H + O₂ + M) has a preferred rate coefficient of $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1 bar N₂ and 300 K (Atkinson et al., 2006). Given an O₂ concentration of between 10^{17} and $10^{18} \text{ molecules cm}^{-3}$, the lifetime of atomic H with respect to reaction with O₂ is less than 10 μs. Any atomic H which doesn't react with O₂ would be more likely to react with any NO₂ ($k =$

$1.47 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; Su et al., 2002), or with HO_2 ($k = 8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; Atkinson et al., 2006), than with the slow reacting aromatic VOC.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J. and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species, *Atmos. Chem. Phys.*, 6, 3265-4055, <https://doi.org/10.5194/acp-6-3625-2006>, 2006. Also at <http://iupac.pole-ether.fr/index.html>.

Su, M.-C., Kumaran, S. S., Lim, K. P., Michael, J. V., Wagner, A. F., Harding, L. B. and Fang, D.-C.: Rate constants $1100 \leq T \leq 2000 \text{ K}$, for $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$ using two shock tube techniques: Comparison of theory to experiment, *J. Phys. A.*, 106, 8261-8270, <https://doi.org/10.1021/jp0141023>, 2002.

10 *Page 12, last paragraph: is it possible that the fact that you do not find agreement between model and observations with increasing NO is due to the fact that you do not consider in your model reactions of RO₂ with NO?*

15 RO_2 reacts with NO with a rate coefficient between approximately 10^{-12} and $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature. This would make the $\text{RO}_2 + \text{NO}$ reaction competitive with the reaction between HO_2 and NO ($k = 8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) under the experimental conditions. The presence of RO_2 could therefore limit the availability of NO for scavenging HO_2 , thereby reducing the amount of VOC reacting with OH. As the simulated results showed a drop in OH + VOC relative to experiments, the addition of RO_2 to the simulations would presumably further exacerbate this. This ignores the fact that RO_2 is only present after initial OH + aromatic reactions, by which time much of the NO would already have been consumed by reaction with HO_2 .

20 The reviewer is correct, however, in that the development of a more comprehensive model, incorporating RO_2 and more extensive secondary chemistry, would be beneficial for elucidation, and further interpretation, of the experimental results and for model reliability.

Figure 1, 2 and 3: I don't understand what the dashed arrows mean? Does it just show the direction of where the data points should go, or has the lengths of the arrow (which is different- in the different figures) a meaning? How did you choose the x-values of these data points? In figure 3 the three red and two green dots are slightly displaced, while in Figure 4 they all have the same x-value. I guess this has no meaning? I would have expected the points on the dashed lines, and maybe the arrows down to the x-axis to indicate the retrieved rate constant. The current version is confusing to me, so please explain in more detail (maybe also in the text, not just in the legend).

30 The authors agree that this is confusing to readers. The inclusion of these data points (for previously unmeasured VOCs) is to illustrate their measured depletion values (y-axis value) relative to the other compounds in the mixture. Their x-values in the figures have no meaning as the x-axis is specifically for literature rate coefficient value (which these compounds do not have). The dashed arrows are there to indicate the points at which these compounds would fall on the OH_{exp} curve. The caption for Figure 2 has been updated to clarify this and now reads "Data for *n*-pentylbenzene (A) was not used in the calculation of OH_{exp} but was included on the plot to illustrate its measured depletion factor." The captions for Figure 3 and Figure 4 were

also updated accordingly. The final sentence for the captions for all three plots already provided an explanation for the use of the dashed arrows. The sentence (which read “The dashed arrows indicate that the k values for the target compounds are determined by where they would fall on the measured OH_{exp} curve.”) has been moved to precede the lists of compounds and follow the sentence amended above.

5 **Anonymous Referee #2**

This is the reviewer report for manuscript entitled “Rate coefficients for reactions of OH with aromatic and aliphatic volatile organic compounds determined by the Multivariate Relative Rate Technique” by Jacob T. Shaw, Andrew R. Rickard, Mike J. Newland and Terry J. Dillon. The paper describes an experimental gas-phase kinetic study of reactions of VOC with OH at 296 K. Particularly, the multivariate relative rate technique, developed by the authors in previous works, was employed here to determine thirty-five rate coefficients, five of which were determined for the first time. The results are in good agreement with available literature values and SAR estimations, which indicates that this methodology is appropriate to determine simultaneously rate coefficients of VOC mixtures with OH. In this work also the sensitivity of this technique was improved and rate coefficients for slower reacting VOC with OH were determined. In my opinion, this paper is well structured and comprehensive and it represents a significant contribution to the atmospheric chemistry. I support publishing the paper after minor corrections suggested below.

The authors would like to thank the referee for their supportive review.

In Section 3.1, Figure S2 is mentioned in the text but Figure S1 is never mentioned in the manuscript. Maybe Figure S1 should be mention in the text of Section 2 (Methodology).

20 Thank you for pointing this out. The text in Section 2 has been amended to refer to Figure S1 at the end of the second sentence (Page 6, Line 4).

Page 8, line 17, Figure S2 is related with Mixture 2 but caption of Figure S2 mentions Mixture 1, it should be checked.

25 The reviewer is correct, Figure S2 should refer to Mixture 2. The text for the caption of Figure S2 has been corrected. The caption for Figure S3 also had the same error and has been corrected.

Figure S4 of the supplemental material (referred to Mixture 3) is never mentioned in the manuscript.

A reference to Figure S4 has been added to the caption for Table 1.

Table 2 caption should be checked because it mentions Figure S3 for Mixture 2, but Figure S3 caption mentions Mixture 1.

30 The caption for Figure S3 has been amended to correctly refer to Mixture 2.

Anonymous Referee #3

The manuscript entitled “Rate coefficients for reactions of OH with aromatic and aliphatic volatile organic compounds determined by the Multivariate Relative Rate Technique” by Shaw et al. reported the rate

coefficients for the 35 VOCs with OH radicals (five of which are measured for the first time) at room temperature by using the recently developed multivariate relative rate technique. The obtained rate coefficients are in reasonable agreement with previously reported values and SAR calculated ones. The paper is very clear and well explained. It should be published after incorporating the minor corrections suggested below.

5 The authors would like to thank the referee for their supportive review.

In Page3, Line 10: What do you mean by five aromatic compounds and eleven aromatic compounds?

10 The reviewer is referring to a section of the main document which currently reads, “The total concentration of five aromatic compounds was measured to be 27 (\pm 8) ppbv in Mumbai (Pandit et al., 2011) while summed concentrations of eleven aromatic compounds were measured to be 30 ppbv in Yokohama City (Tiwari et al., 2010).” This was intended to provide some indication of the prevalence of aromatic compounds in different polluted cities. Comparing values for 5 compounds with 11 compounds, as implied by the sentence, isn’t particularly valid. The sentence has therefore been split in two and rearranged to remove the implied comparison.

In Page 4; Line 10: The author should cite a reference.

15 The authors are unsure which sentence the reviewer is referring to. The sentence on Page 4, Line 10 reads, “In laboratory studies performed at low O₂ concentrations, the competition of these pathways can lead to non-atmospherically relevant product distribution and must be considered (Ji et al., 2017; Newland et al., 2017)” and has two references. The preceding sentence doesn’t have a reference but refers to two numbers in the previous sentence, which are referenced.

20 *What is the rate coefficient for the reaction R2?*

Reaction R2 (H + O₂ + M) has a preferred rate coefficient of 1.0×10^{-12} cm³ molecule⁻¹ s⁻¹ at 1 bar N₂ and 300 K (Atkinson et al., 2006). A reference to this rate coefficient has been added to the manuscript.

25 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J. and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3265-4055, <https://doi.org/10.5194/acp-6-3625-2006>, 2006. Also at <http://iupac.pole-ether.fr/index.html>.

How did the authors confirm the absence of any dark reactions?

30 During configuration of the experimental setup, various experiments were performed to assess the extent of VOC losses to other reactions. “Dark reactions” were tested for by comparing the measured VOC concentrations (GC-MS) for mixtures with and without H₂O in the reactor whilst the lamp was removed. Further tests were conducted to compare the concentrations of VOCs with and without the reactor (i.e. through ¼” stainless steel tubing). The results of these tests showed little variation in VOC concentrations that were well within the instrumentation noise. Regardless, the presence of any reactions that occurred during “dark” experiments (“lamp off”) would not pose a problem as long as they were consistent from “lamp on” to “lamp

off” i.e. if they were always present. Readers are referred to Shaw et al. (2018) and references therein (e.g. Cryer et al. (2016)) at the beginning of the methodology section.

Cryer, D. R.: Measurements of hydroxyl radical reactivity and formaldehyde in the atmosphere, PhD thesis, University of Leeds, 2016.

5 Shaw, J. T., Lidster, R. T., Cryer, D. R., Ramirez, N., Whiting, F. C., Boustead, G. A., Whalley, L. K., Ingham, T., Rickard, A. R., Dunmore, R. E., Heard, D. E., Lewis, A. C., Carpenter, L. J., Hamilton, J. F. and Dillon, T. J.: A self-consistent, multivariate method for the determination of gas-phase rate coefficients, applied to reactions of atmospheric VOCs and the hydroxyl radical, *Atmos. Chem. Phys.*, 18, 4039–4054, <https://doi.org/10.5194/acp-18-4039-2018>, 2018b.

10 *In Page 8, Line 30: Authors should state the percentage depletion of all the studied VOCs other than t-butyl and n-pentyl benzene.*

The authors believe that a list of percentage depletions for 11 VOCs would be difficult to read within the text of the main manuscript. Instead, Table S1, comparing percentage depletions for each VOC in Mixture 2 under different NO conditions, has been added to the Supplementary Information. This table is referred to in on
15 Page 8 Line 32.

In Page 9, Line8: Authors should state the name of the compounds in the running text for the benefit of the readers.

The sentence has been amended to refer readers to Table 3, which contains a list of all compounds in Mixture 3.

20 *In Page 13, Line 20: Cite the reference for the concentration of OH radicals.*

Page 13, Line 20 has been amended to include a reference to Li et al. (2018): “Atmospheric lifetimes for the eight VOCs for which rate coefficients for reaction with OH were measured for the first time, were calculated using a global 24-hour average atmospheric tropospheric concentration of $[OH] = 1 \times 10^6$ molecules cm^{-3} (Li et al., 2018).”

25 Li, M., Karu, E., Brenninkmeijer, C., Fischer, H., Lelieveld, J. and Williams, J.: Tropospheric OH and stratospheric OH and Cl concentrations determined from CH_4 , CH_3Cl , and SF_6 measurements, *npj Clim. Atmos. Sci.*, 1, 29, <https://doi.org/10.1038/s41612-018-0041-9>, 2018.

In Figures 2 and 3, the dashed lines are very much confusing. What does it state? Does it show the rate coefficients? Please give a detailed explanation of this.

30 Please see the authors’ response to comments from Referee #1 above. Hopefully the updated Figure captions provide a more obvious explanation as to the meaning of these arrows.

The caption of Figure S3 should be corrected (mixture 1 should be replaced by mixture 2) as the authors have mentioned mixture 2 in the caption of Table 2.

Please see the authors' response to comments from Referee #2 above. This has been corrected.

Anonymous Referee #4

5 This paper entitled "Rate coefficients for reactions of OH with aromatic and aliphatic volatile organic compounds determined by the Multivariate Relative Rate Technique" by Shaw et al. presents the measurements of 35 rate coefficients at 296 K from the reactions of aromatic and aliphatic volatile organic compounds with OH radicals, using the multivariate relative rate method. This method has been presented for the first time by the same research group in the paper of Shaw et al., ACP, 2018. The experimental work presented in this paper appears to be of very high quality, precise and well presented. The obtained rate coefficients are in good agreement with the evaluated literature, and well supported by SAR. Overall, the paper is well written. I recommend the publication in Atmospheric Chemistry and Physics journal.

The authors would like to thank the referee for their supportive review.

Page 5, line 1: The sentence is too general and is not really specific to the remaining gaps that the present work aims to fill. Please rephrase accordingly

15 We agree that this sentence is quite generic and doesn't fit the context of the paragraph. The sentence has been removed from the manuscript.

Page 9, lines 5-6: The statement that the obtained OH rate coefficients for the ten reactions is in agreement with the those from literature within errors, is not entirely correct. The obtained kOH for n-propylbenzene is not in agreement with the evaluated literature within the indicated errors. Please correct the sentence accordingly.

20 The reviewer is correct that the result for n-propylbenzene does not agree with the literature value (many thanks for pointing this error out). The sentence has been amended to read: "Results for all ten reactions, except that for n-propylbenzene, were in agreement with evaluated literature rate coefficients, within errors."

Page 9, lines 31-32: From the Table 4, the comparison between the measured kOH and the evaluated literature k is not evaluated. Please add a comment.

25 This paragraph has been reorganised slightly and an additional sentence added to compare measured k_{OH} with literature k_{OH}. The paragraph now reads:

30 "A fourth synthetic gas mixture, containing aliphatic VOCs with a range of sizes, branching and OH reaction rate coefficients, was also measured using the multivariate relative rate method. Figure 4 shows the relative rate plot for this VOC mixture. A clear linear relationship was observed between depletion factor and literature rate coefficient. Table 4 provides a list of compounds in this mixture, along with their measured rate coefficient and evaluated literature reference rate coefficient, where available. Results for all seven of the reference reactions were in excellent agreement with evaluated literature rate coefficients, within errors. Rate coefficients for the reactions of OH with three VOCs (2-methylheptane, 2-methylnonane and ethylcyclohexane), were measured for the first time."

Page 27, Figure 4: In contrast to the other plots, the plot showed in Figure 4 is characterized by a higher Y-intercept which might be statistically significant, which represents more than 10% of the maximum measured depletion factor. How do you explain this observation?

Equation 1 (also below) indicates that, when plotting depletion factor ($\ln[\text{VOC}]_0/\ln[\text{VOC}]$) against k_{OH} , the intercept should be zero. Experimental uncertainty means that a non-zero intercept can be acceptable, but the reviewer is correct in asserting that the intercept in Figure 4 may be non-trivial.

A non-linear (curved) relationship between depletion factor and k_{OH} has previously been observed, and was reported in work introducing this technique (Shaw et al., 2018). This relationship was observed to occur for VOC mixtures with a large range in VOC + OH rate coefficients. Poor mixing within the reactor was thought to result in an inconsistent concentration of OH being available for reaction with VOCs, leading to the observed non-linearity. This hypothesis was successfully replicated using kinetic models.

It could be the case that such a relationship occurred for this mixture. With no measurements of VOCs with a k_{OH} value less than $3.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, the relationship below this point is impossible to demonstrate and cannot reliably be extrapolated. In any case, the authors maintain that so long as a consistent function can be plotted through the data to model the depletion factor vs. k_{OH} curve, the actual nature of the relationship is not important when deriving rate coefficients. Extrapolation of the curve should be avoided where possible by using reference reactions which encapsulate the targeted reactions.

$$\ln\left(\frac{[\text{VOC}]_0}{[\text{VOC}]}\right) = k_{\text{VOC}+\text{OH}} \int [\text{OH}]_t dt$$

For more discussion on the non-linearity of these relative rate plots, the reviewers (and readers) are referred to Shaw et al. (2018), and its Supplement and Discussion.

Shaw, J. T., Lidster, R. T., Cryer, D. R., Ramirez, N., Whiting, F. C., Boustead, G. A., Whalley, L. K., Ingham, T., Rickard, A. R., Dunmore, R. E., Heard, D. E., Lewis, A. C., Carpenter, L. J., Hamilton, J. F. and Dillon, T. J.: A self-consistent, multivariate method for the determination of gas-phase rate coefficients, applied to reactions of atmospheric VOCs and the hydroxyl radical, *Atmos. Chem. Phys.*, 18, 4039–4054, <https://doi.org/10.5194/acp-18-4039-2018>, 2018.

Page 11, lines 24-29, Figure 8: The use of higher concentration of O2 tends to improve the accuracy of the results, as shown in Figure 8 and stated in the manuscript, in particularly in reducing the back decomposition of the OH-aromatic adduct. Based on this observation, I wonder why the use of zero air was not considered in the flow reactor, at least, replacing N2 flowing through MFC 2 (see Figure S1), introducing zero air through the mobile injector. Is there any reason that N2 was chosen preferentially?

High purity (grade 6, 99.9999% pure) N₂ was initially chosen to reduce contamination and the potential for further reactive chemistry after the initial oxidation of the primary VOCs. The back decomposition of the intermediate OH-adduct only occurs for aromatic VOCs and not for aliphatic VOCs such as alkanes and alkenes. The high purity N₂ was carried over from the previous primarily aliphatic experiments (Shaw et al., 2018) but the

reviewer is correct in that experiments could be repeated with zero air to better quantify the impact of higher concentrations of O₂.

- 5 Shaw, J. T., Lidster, R. T., Cryer, D. R., Ramirez, N., Whiting, F. C., Boustead, G. A., Whalley, L. K., Ingham, T., Rickard, A. R., Dunmore, R. E., Heard, D. E., Lewis, A. C., Carpenter, L. J., Hamilton, J. F. and Dillon, T. J.: A self-consistent, multivariate method for the determination of gas-phase rate coefficients, applied to reactions of atmospheric VOCs and the hydroxyl radical, *Atmos. Chem. Phys.*, 18, 4039–4054, <https://doi.org/10.5194/acp-18-4039-2018>, 2018.

Page 17, line 13: “www.kinetcus.com” should be replaced by www.kintecus.com

Thank you for pointing this out! This has been corrected.

- 10 *Page 21, line 4: “OH reactivity” should be replaced by “OH reactivities”.*

This has been corrected.

Rate coefficients for reactions of OH with aromatic and aliphatic volatile organic compounds determined by the Multivariate Relative Rate Technique

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Abstract. The multivariate relative rate method was applied to a range of volatile organic compounds (VOC) reactions with OH. This previously published method (Shaw et al., 2018b) was improved to increase the sensitivity towards slower reacting VOC, broadening the range of compounds which can be examined. A total of thirty-five room temperature relative rate coefficients were determined; eight of which have not previously been reported. Five of the new reaction rate coefficients were for large alkyl substituted monoaromatic species recently identified in urban air masses, likely with large ozone production potentials. The new results (with k_{OH} (296 K) values in units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) were: *n*-butylbenzene, 11 (\pm 4); *n*-pentylbenzene, 7 (\pm 2); 1,2-diethylbenzene, 14 (\pm 4); 1,3-diethylbenzene, 22 (\pm 4) and 1,4-diethylbenzene, 16 (\pm 4). Interestingly, whilst results for smaller VOC agreed well with available structure activity relationship (SAR) calculations, the larger alkyl benzenes were found to be less reactive than the SAR prediction, indicating that our understanding of the oxidation chemistry of these compounds is still limited. k_{OH} (296 K) rate coefficients (in units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for reactions of three large alkanes with OH were also determined for the first time: 2-methylheptane, 9.1 (\pm 0.3); 2-methylnonane, 11.0 (\pm 0.3) and ethylcyclohexane, 14.4 (\pm 0.3), all in reasonable agreement with SAR predictions. Rate coefficients for the twenty-seven previously studied OH + VOC reactions agreed well with available literature values, lending confidence to the application of this method for the rapid and efficient simultaneous study of gas-phase reaction kinetics.

15

1 Introduction

The troposphere contains many thousands of organic compounds (Lewis et al., 2000; Goldstein and Galbally, 2007). These compounds differ substantially in their chemical and physical properties. Volatile organic compounds (VOC) are organic chemicals which take part in photochemical degradation cycles leading to the formation of ground-level ozone and photochemical smog, and the production of secondary organic aerosols – significantly impacting upon air quality and climate.

Aromatic VOC can account for a large proportion of the non-methane hydrocarbon mass in the atmosphere. At least ninety different aromatic compounds have been identified in diesel fuel (Hamilton and Lewis, 2003). Aromatics are therefore particularly prevalent in heavily urbanised environments associated with large amounts of fuel combustion and solvent use. For example, aromatic VOCs were reported to account for up to 33% of the VOC emission mass from vehicle exhausts in China (Guo et al., 2011; Cao et al., 2016). Summed concentrations of eleven aromatic compounds were measured to be 30 ppbv in Yokohama City (Tiwari et al., 2010). In Mumbai, ~~the total concentration of five aromatic compounds was measured to be 27 (± 8) ppbv in Mumbai (Pandit et al., 2011), while summed concentrations of eleven aromatic compounds were measured to be 30 ppbv in Yokohama City (Tiwari et al., 2010).~~ Peak concentrations of aromatic VOCs can be much greater, however; Dunmore et al. (2015) measured daily winter-time peaks for monoaromatics containing four carbon atoms as part of ~~alkyl substituents (henceforth C₄ aromatics) substituted monoaromatics~~ of 500 ppbv, associated with extensive traffic pollution in London.

Whilst many aromatic species are known to exist in the atmosphere, measurements of OH + aromatic VOC rate coefficients are sparse. The IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation provides evaluated rate coefficients for twenty-six OH + aromatic reactions, including cresols, phenols, nitrophenols, quinones and furans (Atkinson et al., 2006). Calvert et al. (2002) provides an evaluation of a further eighteen reactions between OH and aromatic VOCs with alkyl substituents. More recently, Jenkin et al. (2018a) have developed an updated aromatic + OH structure-activity relationship (SAR) based on a compiled database of sixty-seven monocyclic aromatic hydrocarbons and oxygenated organic compounds, including eight higher alkyl-substituted benzenes and four alkenylbenzenes. Despite their ubiquity in the urban atmosphere, repeat measurements of OH + aromatic VOC rate coefficients by different laboratories are rare; only toluene, *o*- and *m*-xylene and the three isomers of trimethylbenzene have five or more example measurements in the literature. The number of available rate coefficient measurements drastically decreases with increasing substituent size of aromatic VOCs.

The propensity for VOCs to generate tropospheric ozone through their photochemical oxidation is indicated by their photochemical ozone creation potentials (POCP). This model calculated reactivity index describes the relative capability for an organic compound to produce ozone over north-west Europe (Derwent et al., 1998, 2007). ~~Di- and tri-~~ substituted Monoaromatics with two, or three alkyl, substituents, containing one, two, or three carbon atoms (henceforth C₁, C₂ and C₃ aromatics) have relatively large POCP values meaning that they are amongst the emitted species with the greatest potential for producing ozone (Derwent et al., 2007).

Many measurement techniques fail to detect aromatic compounds with larger alkyl substituents (greater than three carbons) and are therefore limited to quantifying the smaller substituted aromatics, such as toluene, xylenes, and trimethylbenzenes. In the absence of measured values, toluene-equivalency ratios can provide a prediction of the additional aromatic content of the atmosphere based on measured concentrations of the smaller aromatic compounds (Lidster et al., 2014).

5 However, using toluene concentration as a proxy for concentrations of larger aromatics requires knowledge of their rate coefficient for reaction with OH; this is often unavailable for C₄ and larger aromatics.

Reactions between aromatic VOCs and the hydroxyl radical (OH) primarily involve OH addition to the aromatic ring. For benzene, and the methyl- and ethyl-substituted aromatics this pathway dominates at room temperature, accounting for greater than 90% of the OH reaction. The reaction produces a hydroxyalkylcyclohexadienyl radical, or OH-aromatic adduct, which can decompose back to VOC + OH, or be captured by reaction with O₂ or NO₂. Pseudo first-order rate coefficients for the OH-adduct + O₂ capture reaction, and for the OH-adduct back decomposition, are 1000 s⁻¹ and 1 s⁻¹ respectively at [O₂] = 0.2 atm (Vereecken et al., 2019). Thus, while in the troposphere, effectively all of the OH-adduct is captured by reaction with O₂. In laboratory studies performed at low O₂ concentrations, the competition of these pathways can lead to non-atmospherically relevant product distribution and must be considered (Ji et al., 2017; Newland et al., 2017). The OH-adduct can also react with NO₂, but the ratio of the O₂ and NO₂ rate coefficients is such that, under typical atmospheric conditions, monocyclic aromatics react almost exclusively with O₂ (Knispel et al., 1990; Koch et al., 1994; Bohn and Zetzsch, 1999; Bohn, 2001). Meta-substituted aromatics, such as *m*-xylene, react faster than their ortho- and para- counterparts owing to enhanced electrophilic addition of OH leading to the formation of a resonance stabilised tertiary radical addition product (Ravishankara et al., 1978; Nicovich et al., 1981; Mehta et al., 2009). Arrhenius plots for the reactions of VOCs with OH tend to exhibit complex behaviour; two distinct regions are visible over a large temperature range. It is thought that the OH-aromatic adduct undergoes thermal decomposition at temperatures greater than 325 K, so that the H-atom abstraction pathway becomes the dominant reaction mechanism as temperature increases. The atmospheric lifetime of the OH-aromatic adduct is predicted to be approximately 0.3 s at 298 K (Atkinson and Arey, 2003). This decreases rapidly with temperature to an approximate lifetime of 20 μs at 450 K. To gain a thorough understanding of the oxidation of aromatic VOCs, these reactions need to be studied across the typical range of atmospheric conditions.

Alkanes are also ubiquitous in the urban atmosphere and are generally associated with vehicle emissions. Approximately 40% of the chemicals found in exhaust emissions are alkanes (Guo et al., 2011; Cao et al., 2016) but this can increase to up to 90% when the engine loading is above 30% (Pereira et al., 2017). Long-chain diesel related aliphatic hydrocarbon species (C₁₀-C₁₃) have been observed to dominate the gas phase reactive carbon in cities with high diesel fleet fractions (Dunmore et al., 2015) and have also been detected in engine exhaust (Erickson et al., 2014).

The relative rate method is an established technique for the measurement of rate coefficients for the reactions of VOCs with OH. Recent developments in the analytical capabilities of instrumentation have allowed for the development of an extension to the technique, in which multiple reactions can be monitored simultaneously (Shaw et al., 2018a; Shaw et al., 2018b). Rather than measuring a target reaction relative to a single reference reaction, target reactions are placed on an absolute

basis relative to a suite of similar reference reactions, reducing the reliance on using any single value as a reference. This multivariate technique has been used to measure the rates of reaction for nineteen VOC with OH at room temperature, and for twenty-five VOC (twelve of which were aromatic VOC) with OH at an elevated temperature of 323 (\pm 10) K (Shaw et al., 2018b).

5 ~~Clearly there remain significant gaps in our understanding of atmospheric oxidation chemistry. Accordingly, i~~In this work, laboratory based experiments were conducted to study the gas-phase kinetics of a suite of atmospherically important reactions of aromatic and aliphatic VOCs with OH. Use of the multivariate relative rate technique allowed the rapid determination of thirty-five ~~such~~ rate coefficients (k_{OH} (296 K)) including for C₃ and C₄ mono-substituted benzenes, a range of diethylbenzene isomers, and a number of methyl- and ethyl-branched alkanes that were, to the best of our knowledge,
10 previously unknown.

2 Methodology

A detailed description of the multivariate relative rate technique was provided in Shaw et al. (2018b). Briefly, three synthetic gas-mixtures were prepared by injecting 1–7 mm³ of undiluted VOC into a 500 cm³ evacuated sample cylinder (Swagelok) and flushing through into a pacified gas-cylinder (10 L, Experis, Air Products) with N₂ (Fig. S1). A two-stage dilution process was required to achieve approximate mixing ratios of each VOC in the cylinder of 40 parts per billion by volume (ppbv). Gas-phase reactants were mixed in a flow reactor under conditions of 1 bar (N₂) and 296 (± 2) K. Photochemical oxidation reactions were initiated through the use of a low-pressure Hg/Ar lamp (L.O.T., Pen-Ray®); OH radicals were generated by the photolysis of H₂O via Reaction (R1). It was expected that the atomic H by-product was rapidly converted to HO₂ by reaction with molecular oxygen, which could not be fully excluded from the reactor (R2; $k_2 = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1 bar N₂ and 300 K; Atkinson et al., 2006).



To limit photolysis of the aromatic VOC, by either the 185 nm emission or by the principal Hg emission band at 254 nm, the gas mixture was introduced into the reactor downstream of the photolysis zone via a moveable injector (Cryer, 2016; Shaw et al., 2018a). Depletion of VOC due to photolysis was not observed for mixtures containing *m*- and *o*-xylene (Shaw et al., 2018a). Flow rates of the VOC gas mixture and the diluting N₂ bath gas containing H₂O were controlled by various mass flow controllers (MKS and Tylan). Assuming a constant total flow rate of 3000 cm³ min⁻¹ into the reactor, the VOC were estimated to have a residence time of 4 s, of which OH was estimated to persist for no longer than 0.5 s.

Samples were collected with the lamp alternately switched off and on, thereby generating two datasets; one in which the VOC concentrations were representative of their cylinder concentration, and one in which the VOC concentrations were depleted by reaction with OH. The depletion factor for a VOC due to reaction with OH ($\ln \left(\frac{[\text{VOC}]_0}{[\text{VOC}]} \right)$) was related to its rate coefficient for reaction with OH by Eq. (1) (Shaw et al., 2018a). The integral of OH concentration as a factor of time is referred to as the OH exposure (OH_{exp}); all VOC in the gas mixture should experience identical exposure to OH radicals. By simultaneously measuring depletion factors for a range of VOC with different reactivities towards OH, the system was calibrated with respect to rate coefficient. A rate coefficient value for the reaction between each VOC and OH could then be calculated relative to all other reactions, by placing the depletion factor vs k relationship on an absolute basis.

$$\ln \left(\frac{[\text{VOC}]_0}{[\text{VOC}]} \right) = k_{\text{VOC}+\text{OH}} \int [\text{OH}]_t dt \quad (1)$$

Producing OH via the photolysis of H₂O also resulted in the production of HO₂ (R2). Although HO₂ is much less reactive towards VOCs than OH, it may represent a significant OH sink within the reactor via Reaction (R3). The recommended rate coefficient for this reaction is $k_3 = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006); thus this reaction may proceed at a rate fast enough to compete with the VOC for OH.

5



Whilst this was not an issue with the synthetic gas mixtures measured in Shaw et al. (2018b), some of the mixtures in this work contained slower reacting VOC. Hence, the HO₂ may outcompete the VOCs for OH, resulting in only negligible depletions in the VOC concentrations.

10 The impact of HO₂ was minimised by adding NO into the reactive mix. This served two purposes. Firstly, NO reacts with HO₂ (R4) with a recommended rate coefficient of $k_4 = 8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006). Although this value is much smaller than that for the HO₂ + OH reaction, the addition of significant quantities of NO reduced the amount of OH lost to reaction with HO₂. Secondly, one of the products of the HO₂ + NO reaction is OH. This reaction therefore served
15 as a secondary source for OH radicals, effectively converting the photolysis by-product (HO₂) into useful OH.



The GC-MS system used for chromatographic separation and detection was an Agilent 6890 (Agilent Technologies)
20 fitted with a DB5-MS ultra-inert capillary column (60 m × 0.32 mm ID × 1 μm film, Agilent Technologies), coupled to a Markes International BenchTOF© mass spectrometer. The temperature ramping in the GC oven varied between mixtures to optimally resolve all mixture components; the sample turnarounds, across both GC method and TDU setup, was approximately 20 min. For a full description of the gas sampling and analysis, please refer to Shaw et al. (2018b).

3 Results and discussion

Experimental results from four synthetic gas mixtures containing aromatic VOCs are presented in Sect. 3.1. Results and conclusions drawn from numerical simulations are presented in Sect. 3.2. All errors presented in this work represent 1σ (66%) and account for the statistical uncertainties calculated by combining the instrument error and the scatter in the relative rate plots. It is worth noting that the uncertainties quoted on the evaluated literature reference values are often large (up to 35% of the measured value); using these values to place the measured data on an absolute basis therefore limits the final precision of the results in this work. These limitations may not be captured by the quoted uncertainties.

3.1 Results from relative rate experiments at 296 K

The measured depletion factor for each VOC in Mixture 1 was plotted against their evaluated rate coefficients using Eq. (1) (Figure 1). This demonstrates the typical linear relationship between depletion factor and rate coefficient. Mixture 1 contained several aromatic VOCs with multiple methyl substituents, such as the three trimethylbenzene isomers and two isomers of tetramethylbenzene. Multiple, well-evaluated reference reactions (OH + isoprene, OH + pinenes, OH + xylenes) were included as part of this mixture to place the relative rate values on a reliable absolute scale. The rate coefficient results for this mixture are provided in Table 1. All of the measured values were in excellent agreement with the evaluated literature rate coefficients. In particular, the results for the tetramethylbenzene + OH reactions were in good agreement with their literature counterparts, despite their only being measured once or twice previously (Aschmann et al., 2013; Alarcón et al., 2015).

Figure S2 shows sections of typical ion chromatograms (TIC) obtained for Mixture 2: one chromatogram with the reactor lamp turned off (blue) and one for a sample with the reactor lamp turned on (black). There was a clear, but small, reduction in the peak areas observed with the lamp on relative to the lamp off, corresponding to the depletion in the VOCs due to reaction with OH. Figure S2 also shows that the observed reduction for the peak assigned to *n*-pentylbenzene was negligible.

Figure 2 shows the relative rate plot for Mixture 2 (see Table 2) with an OH reactivity (in the reactor) of approximately 18 s^{-1} . A linear relationship between depletion factor and k was observed but the scale of the depletion factor was exceptionally low when compared with similar plots for more reactive mixtures (such as Mixture 1 (Fig. 1) or those in Shaw et al., 2018b). Typically, when using synthetic mixtures containing relatively fast reacting isoprenoid species such as monoterpenes, the measured depletion factors were greater than 0.1 for all VOCs. The depletion factors measured here were equivalent to depletions of less than a few percent; for example, *t*-butyl- and *n*-pentylbenzene recorded depletions of just 0.3% and 0.2% respectively. These small depletions were attributed to the presence of HO₂ within the reactor, which represented a greater sink for OH than the VOCs themselves, given their relatively slow reactions with OH.

In an attempt to increase the depletion factor, NO was added to the reactor to convert HO₂ to OH (see reaction R4). There was an observed increase in the measured depletion factors for each of the VOCs corresponding with the increased [NO] in the reactor. The percentage depletions in *t*-butyl- and *n*-pentylbenzene increased to 2.3% and 3.0% respectively when using [NO] = 70 ppb (see Table S1). The addition of NO to the system therefore resulted in increased VOC depletions; this was

especially useful for the slowest reacting VOCs, for which the observed depletions were often below the limit of detection in the absence of NO.

Table 2 provides the estimated rate coefficient values for the reaction of each VOC in Mixture 2 with OH, as calculated using Eq. (1). Measured k values are provided for each of the three experiments using different NO concentrations together with an overall weighted mean for each of the VOC + OH reactions. Results for each of all the ten reactions, except that for *n*-propylbenzene, were in agreement with evaluated literature rate coefficients, within errors. The rate coefficient for *n*-pentylbenzene + OH, $k_{\text{OH}}(296 \text{ K}) = 5.3 (\pm 0.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is one of two determinations reported in this study.

Figure 3 shows the results from a third mixture comprising 10 aromatic VOCs and three simple linear and branched alkanes (Table 3). The alkanes were used as well-characterised reference reactions to assist with the diagnosis of the depletion factor vs rate coefficient trend. The final results for this mixture are provided in Table 3. All measured rate coefficients were in agreement with their corresponding evaluated literature values. The measured rate coefficient for the *n*-propylbenzene + OH reaction was larger than the evaluated literature counterpart by approximately 20% but was consistent within errors. This mixture contained a homologous series of mono-substituted aromatic VOC with an increasing alkyl-substituent chain length, from toluene ($\text{C}_6\text{H}_5\text{CH}_3$) to *n*-pentylbenzene ($\text{C}_6\text{H}_5(\text{CH}_2)_4\text{CH}_3$). The results for this series of reactions show that the rate coefficient increased with increasing number of carbon atoms in the aryl group up to four carbon atoms, although the measurement for $k_{\text{OH}+n\text{-butylbenzene}}$ had a large derived uncertainty. The rate coefficient for reaction with OH then decreased with the addition of the extra carbon atom from *n*-butylbenzene to *n*-pentylbenzene. The rate coefficient for the *n*-butylbenzene + OH has not been measured previously. The rate coefficient for the *n*-pentylbenzene + OH, $k_{\text{OH}}(296 \text{ K}) = 7 (\pm 2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is in agreement with the same measurement in Mixture 2, within 1σ uncertainties.

Mixture 3 included the three isomers of diethylbenzene ($\text{C}_6\text{H}_5(\text{CH}_2\text{CH}_3)_2$), for which no literature rate coefficients for reactions with OH could be found at the time of writing. The averaged measured values, from the five different OH reactivities tested, were ($k_{\text{OH}}(295 \text{ K})$ in units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): 1,2-diethylbenzene, $k = 14 (\pm 4)$; 1,3-diethylbenzene, $k = 22 (\pm 4)$ and 1,4-diethylbenzene, $k = 16 (\pm 4)$. Values reported here for the diethylbenzene + OH reactions were extrapolated from the depletion factor vs. k relationship; their measured depletions were all greater than the depletion in the fastest reacting reference compound. There may therefore be a larger extent of uncertainty in their values than that calculated, as the OH_{exp} trend beyond *o*-xylene was unmeasured.

A fourth synthetic gas mixture, containing aliphatic VOCs with a range of sizes, branching and OH reaction rate coefficients, was also measured using the multivariate relative rate method. Figure 4 shows the relative rate plot for this VOC mixture. A clear linear relationship was observed between depletion factor and literature rate coefficient. Table 4 provides a list of compounds in this mixture, along with their measured rate coefficient and evaluated literature reference rate coefficient, where available. Results for all seven of the reference reactions were in excellent agreement with evaluated literature rate coefficients, within errors. Rate coefficients for the reactions of OH with three VOCs (2-methylheptane, 2-methylnonane and ethylcyclohexane), were measured for the first time. ~~Table 4 provides a list of compounds in this mixture, along with their measured rate coefficient and evaluated literature reference rate coefficient, where available.~~

3.2 Comparisons to structure activity relationships

Structure activity relationships (SARs) provide a method for estimating rate coefficients and branching ratios for the reactions of compounds based on their structural properties. SAR derived parameters, when based on large subsets of the kinetic catalogue, may be used as comparisons for the measured values in this work in the absence of, or in parallel with, literature experimental results (Vereecken et al., 2018). Recently, Jenkin et al. (2018a) developed an updated SAR for estimating rate coefficients for reactions of aromatic organic compounds with OH. The SAR was based on a preferred data set of kinetic measurements for twenty-five monocyclic and forty-two oxygenated aromatic hydrocarbons, and returned results with no significant bias, and an average uncertainty of 15% relative to the observational dataset; hence providing a reasonably accurate representation of aromatic reactivity with OH. A similarly constructed SAR, for the estimation of rate coefficients for reactions involving aliphatic compounds, can be found in Jenkin et al. (2018b).

Figure 5 provides a comparison between the measured rate coefficients from this work and the calculated rate coefficients from Jenkin et al. (2018a) (for the reactions of aromatic VOCs with OH), and Jenkin et al. (2018b) (for the reactions of aliphatic VOCs with OH). All of the values measured using the multivariate relative rate technique were in good agreement with those estimated by the SARs. This provides additional validation of the SARs proposed in Jenkin et al. (2018a and 2018b). The five reactions involving aromatic compounds for which no literature measured values existed at the time of writing, were also in good agreement with those estimated using the SAR. Table S42 provides additional SAR derived parameters for these five aromatic reactions, and the three newly measured aliphatic reactions, using alternative SARs described by Kwok and Atkinson (1995) and Ziemann and Atkinson (2012). These SARs performed relatively poorly when simulating the aromatic + OH reaction rate coefficients but performed well for the aliphatic + OH reaction rate coefficients.

Figure 6 shows a more detailed analysis of the measured k_{OH} (295 K) values for the reactions between OH and a homologous series of *n*-alkylbenzenes. Measurements from this work, and a previous study utilising the multivariate relative rate technique, are shown alongside the trend predicted by the Jenkin et al. (2018a) SAR. The SAR generally predicts a small increase in rate coefficient with increasing chain length. Many of the experimental results were in agreement with the SAR when accounting for uncertainties.

Figure 7 shows a similar plot for comparison of the measured rate coefficients for the diethylbenzene isomers with those predicted by the Jenkin et al. (2018a) SAR. This plot further illustrates the good agreement between experimental results from this work and the rate coefficients estimated using the SAR. The experimental results were marginally greater than the predicted values but were in agreement when accounting for uncertainties, despite the lack of previous literature measurements for the diethylbenzene compounds. The proposed aromatic OH SAR presented in Jenkin et al. (2018a) therefore agrees well with the measurements for all aromatic compounds measured as part of this work.

3.2 Interpretations from numerical simulations

Numerical simulations were conducted to aid in the evaluation of the experimental results obtained as part of this work for the aromatic systems. Simulations were performed using the Kintecus software package (Ianni, 2017).

The first set of simulations aimed to assess the significance of the thermal decomposition of the OH-aromatic adducts (as depicted in Figure S55) at different temperatures (Calvert et al., 2002). The chemical model for these simulations used Arrhenius expressions for the initial reactions of OH with benzene, toluene, and *m*- and *p*-xylene (Atkinson and Arey, 2003; Atkinson et al., 2006). The chemical scheme included two subsequent pathways; one in which the OH-aromatic adducts decayed back into the initial aromatics (and OH), and one in which they reacted with O₂. Arrhenius expressions for each of these reactions were included in the model (Perry et al., 1977; Knispel et al., 1990; Koch et al., 2007). Minor H-atom abstraction pathways were neglected. The initial OH concentration was kept constant at 2×10^{11} molecules cm⁻³. The concentration of O₂ within the experimental reactor was not measured experimentally so an estimate of 1×10^{17} molecules cm⁻³ of O₂ (equivalent to an N₂ purity of approximately 99%) was used during the simulations.

Allowing for the decay of the OH-aromatic adduct (at $T = 300$ K) resulted in the correctly simulated relationship between depletion factor and literature k_{OH} value for all four aromatic species, with an R² value of 0.9995. Figure 8 shows that this relationship was sensitive to the concentration of O₂ in the simulation, with the R² value decreasing to 0.856 at $[O_2] = 1 \times 10^{15}$ molecules cm⁻³. Therefore, at the experimental temperature ($T = 296$ K), significant back-decomposition of the OH-aromatic adduct should have been avoided, given the assumed 1% O₂ content (10^{17} molecules cm⁻³) within the reactor.

At elevated temperatures (e.g. $T = 350$ K), the decay of the aromatic adducts proceeds at a quicker rate. The relationship between depletion factor and literature k value was poorly simulated, even when using the assumed concentration of O₂. The simulated depletion factors for some of the aromatic species were also well below the limit of detection for experimental observations, owing to the rapid reformation of the original aromatic species. This suggests that there is a threshold temperature above which significant thermal decomposition of the OH-aromatic adducts would occur, limiting the potential for experimental results.

The thermal instability of the primary product of the aromatic + OH reactions therefore complicated the relative rate nature of these experiments. The potential reformation of the original aromatic species meant that their measured concentrations after reaction with OH may not have been dependent on just their rate coefficient for reaction with OH. However, the numerical simulations performed as part of this work yielded an important conclusion: at the reactor temperatures used during experimentation, the extent of OH-aromatic decay was largely insignificant as long as approximately 10^{17} molecules cm⁻³ of O₂ were present in the reactor, which is assumed to be the case.

A second set of simulations were performed to model the impact that NO had on the chemical mechanisms occurring within the reactor. The chemical scheme for these simulations incorporated the oxidation of the aromatic compounds toluene, ethylbenzene, *n*-propylbenzene, isopropylbenzene, *m*- and *o*-xylene and 2-, 3- and 4-ethyltoluene, as adapted from the Master Chemical Mechanism (Jenkin et al., 2003; Bloss et al., 2005). All reactions involving O₃ and NO₃ were removed from the

chemical model as these oxidants were assumed to be absent from the experimental reactor. Reactions involving RO_2 were also removed from the chemical model for simplification reasons. Basic HO_x/NO_x chemistry was included to yield a simplified chemical scheme comprising a total of 160 reactions and 88 different species.

Reactions involving primary OH (henceforth referred to as *pOH*) were separated from reactions involving secondary OH (*sOH*) within the model. *pOH* corresponds to the OH generated as a direct result of H_2O photolysis. *sOH* refers to the OH generated as a result of the reaction between NO and HO_2 (R4).

Figure S66 shows that adding NO to the reactor increased the simulated extent of aromatic VOC depleted through reactions with OH. A total of 6.1% of the total aromatic VOC reacted with OH in the case without NO compared to 8.2% in simulations with 30 ppb of NO. This correlated well with evidence from experiments in which the depletion factors for individual VOCs increased after the addition of NO to the reactor. However, the simulated proportion of reacted VOC decreased after addition of 70 ppb of NO. This was not observed experimentally. This may suggest that there is an optimum amount of NO to include in the reactor, above which the sinks of OH to reactions with NO and NO_2 begins to dominate. This critical point was not surpassed experimentally, hence leading to the observed trend where increased [NO] led to an increase in depletion factor.

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4 Atmospheric implications and conclusions

The multivariate relative rate technique was successfully adapted to measure the relative reaction rates of twenty different mono-aromatic VOC with OH (at 296 K). Fifteen of these reactions have had rate coefficients reported at least once previously, with the measurements reported here in good agreement with this existing limited experimental dataset. Five of the measured rate coefficients are reported for the first time. These are (in units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): *n*-butylbenzene, $11 (\pm 4)$; *n*-pentylbenzene, $7 (\pm 2)$; 1,2-diethylbenzene, $14 (\pm 4)$; 1,3-diethylbenzene, $22 (\pm 4)$ and 1,4-diethylbenzene, $16 (\pm 4)$. The OH rate coefficients for 12 straight and branched chain aliphatic species were also measured using the multivariate relative rate technique, three of which are not available in the literature. The measured OH reaction rate coefficients for these were (in units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): 2-methylheptane, $9.1 (\pm 0.3)$; 2-methylnonane, $11.0 (\pm 0.3)$ and ethylcyclohexane, $14.4 (\pm 0.3)$. The 296 K measurements were in agreement with the available, but often limited, experimental dataset.

Measurements of slower reactions (relative to many of those measured in Shaw et al., 2018b) proved difficult owing to the limited depletions observed for some of the VOCs. A simple chemical modification to the basic setup successfully increased the extent of the measured depletions allowing for the evaluation of the rates of reaction for slower reacting compounds. The addition of NO to flow reactors is therefore advised for any future work performing this type of self-consistent, multivariate relative rate measurement, particularly when the rates of reaction for the targeted reactive species are below $2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Model sensitivity simulations on the thermal stability of the OH-aromatic adduct intermediate species suggested that there should be limited decomposition to reform the original aromatic precursors under the applied experimental conditions.

Atmospheric lifetimes for the eight VOCs for which rate coefficients for reaction with OH were measured for the first time, were calculated using a [global](#) 24-hour average ~~atmospheric-tropospheric~~ concentration of $[\text{OH}] = 1 \times 10^6 \text{ molecules cm}^{-3}$ (Li et al., 2018). Estimated lifetimes due to reaction with OH (τ_{OH}) for the five aromatic compounds were: *n*-butylbenzene, 25 hours; *n*-pentylbenzene, 40 hours; 1,2-diethylbenzene, 20 hours; 1,3-diethylbenzene, 13 hours and 1,4-diethylbenzene, 17 hours. Given that these aromatic compounds are relatively large and react rapidly with OH (when compared with toluene), they would be expected to have reasonably high photochemical ozone creation potentials (POCPs). Estimated lifetimes due to reaction with OH for 2-methylheptane, 2-methylnonane and ethylcyclohexane were 31, 25 and 19 hours respectively. It should be noted that the lifetimes indicated here have limited applicability in atmospheric environments with substantially different OH concentrations, and that they may be as short as a few hours in environments with particularly high concentrations of OH. Comprehensive chemical modelling would need to be undertaken to fully understand the behaviour of these compounds in different environments, but this is beyond the scope of this work.

The majority of the rate coefficients measured as part of this work were in good agreement with the recently developed SARs by Jenkin et al. for estimating aromatic and aliphatic OH kinetics (Jenkin et al., 2018a; Jenkin et al., 2018b) validating the use of theoretical calculation of OH rate coefficients for reactions involving these compounds. This work highlights that more experimental and theoretical work is required to understand the OH oxidation kinetics and mechanisms of high alkyl

substituted aromatic hydrocarbons in order to extend the kinetic database for more accurate SAR parameter estimations and to assess their impact on atmospheric composition.

Data availability

Raw data is available upon request.

Author contribution

ARR and TJD planned the overall project; JTS and TJD designed experiments; JTS conducted all experiments and performed
5 the analysis; JTS and TJD prepared the manuscript with contributions from all authors.

Competing interests

The authors declare that they have no conflict of interest.

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Tables

Table 1: Results of relative rate experiments, with evaluated literature data, for each VOC in Mixture 1, ordered by evaluated literature k value. The measured values presented here are the weighted averages of five individual experiments conducted with different mixture OH reactivities (see Figure S4).

Name	Measured k (296 K) / $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Evaluated literature k (298 K) / $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Reference	Number of literature measurements
Isoprene	102 ± 4	$100 (\pm \frac{1}{5})$	Atkinson et al., 2006	25+
β -pinene	74 ± 8	79 ± 20	Atkinson and Arey, 2003	10
1,2,3,5-tetramethylbenzene	62 ± 9	62.4 ± 0.8	Alarc3n et al., 2015	1
1,3,5-trimethylbenzene	60 ± 5	57 ± 11	Calvert et al., 2002	5
1,2,4,5-tetramethylbenzene	59 ± 12	55.5 ± 3.4	Aschmann et al., 2013	2
α -pinene	53 ± 8	$53 (\pm \frac{7}{13})$	Atkinson et al., 2006	9
1,2,4-trimethylbenzene	34 ± 3	33 ± 8	Calvert et al., 2002	5
1,2,3-trimethylbenzene	38 ± 4	33 ± 8	Calvert et al., 2002	5
<i>m</i> -xylene	21 ± 3	23 ± 3	Calvert et al., 2002	15
<i>o</i> -xylene	10 ± 4	13 ± 3	Calvert et al., 2002	10

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Table 2: Results of relative rate experiments, with evaluated literature data, for each VOC in Mixture 2, ordered by evaluated literature k value. The results of experiments using different concentrations of NO are presented, along with a mean measured k value for each VOC, weighted to the errors in the individual NO experiments. Each iteration with a different [NO] comprised three individual experiments with different OH reactivities of mixture injected into the reactor. Figure S3 shows the relative rate plots for Mixture 2 with an OH reactivity (in the reactor) of 18 s^{-1} and NO concentrations of 0, 30 and 70 ppb.

5

Name	Measured k (296 K) / $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$			Weighted average	Evaluated literature k (298 K) / $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Reference	Number of literature measurements
	[NO] = 0 ppb	[NO] = 30 ppb	[NO] = 70 ppb				
<i>m</i> -xylene	20.6 ± 0.7	19.6 ± 0.4	19.8 ± 1.3	19.9 ± 0.5	23 ± 3	Calvert et al. 2002	15
3-ethyltoluene	19.7 ± 0.9	21.7 ± 0.4	19.4 ± 1.0	21.1 ± 1.2	19 ± 7	Calvert et al. 2002	2
<i>o</i> -xylene	12.3 ± 1.3	12.4 ± 0.4	12.3 ± 0.6	12.4 ± 0.1	13 ± 3	Calvert et al. 2002	10
4-ethyltoluene	14 ± 2	14.8 ± 0.5	14.1 ± 1.2	14.6 ± 0.3	12 ± 4	Calvert et al. 2002	2
2-ethyltoluene	13.4 ± 1.0	15.0 ± 1.1	12.7 ± 0.1	12.7 ± 0.2	12 ± 4	Calvert et al. 2002	2
Ethylbenzene	5 ± 2	6.0 ± 0.3	6.7 ± 0.5	6.1 ± 0.4	7.0 ± 2	Calvert et al. 2002	3
Isopropylbenzene	6.5 ± 0.5	6.4 ± 0.4	6.5 ± 0.6	6.45 ± 0.02	6.3 ± 2	Calvert et al. 2002	3
<i>n</i> -propylbenzene	8.9 ± 0.7	8.7 ± 0.6	7 ± 2	8.7 ± 0.5	5.8 ± 1.5	Calvert et al. 2002	3
Toluene	5 ± 2	0 ± 2	7 ± 2	4 ± 4	5.6 (± 1.5)	Atkinson et al. 2006	18
<i>t</i> -butylbenzene	3.5 ± 1.1	3.4 ± 0.5	3.1 ± 0.7	3.3 ± 0.1	4.5 ± 2	Calvert et al. 2002	2
<i>n</i> -pentylbenzene	3 ± 5	5.4 ± 0.4	1 ± 4	5.3 ± 0.7			

Table 3: Results of relative rate experiments, with evaluated literature data, for each VOC in Mixture 3, ordered by evaluated literature k value. The measured values presented here are the weighted averages of five individual experiments conducted with different mixture OH reactivities and 40 ppbv NO. Five VOCs had no reported data for their reactions with OH.

Name	Measured k (296 K) / $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Evaluated literature k (298 K) / $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Reference	Number of literature measurements
<i>o</i> -xylene	13.0 ± 1.2	13 ± 3	Calvert et al. 2002	10
2-ethyltoluene	12.2 ± 0.8	12 ± 4	Calvert et al. 2002	2
<i>n</i> -decane	10.7 ± 0.7	11 ± 2	Atkinson, 2003	6
<i>n</i> -nonane	10.1 ± 1.2	10 ± 2	Atkinson, 2003	9
Ethylbenzene	6.6 ± 0.5	7 ± 2	Calvert et al. 2002	3
<i>n</i> -propylbenzene	6.8 ± 0.3	5.8 ± 1.5	Atkinson, 2003	3
Toluene	4 ± 2	$5.6 (^+ \pm 2)$	Atkinson et al., 2006	18
2,2,3-trimethylbutane	6 ± 6	3.8 ± 1.0	Atkinson, 2003	6
1,3-diethylbenzene	22 ± 4			
1,4-diethylbenzene	16 ± 4			
1,2-diethylbenzene	14 ± 4			
<i>n</i> -butylbenzene	11 ± 4			
<i>n</i> -pentylbenzene	7 ± 2			

Table 4: Results of relative rate experiments, with evaluated literature data, for each VOC in Mixture 4, ordered by evaluated literature k value.

Name	Measured k (295 K) / $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Evaluated literature k (298 K) / $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Reference	Number of literature measurements
Cyclooctane	13.7 ± 0.3	13 ± 7	Atkinson, 2003	2
<i>n</i> -undecane	12.3 ± 0.3	12 ± 2	Atkinson, 2003	2
Cycloheptane	11.4 ± 0.3	12 ± 3	Atkinson, 2003	3
<i>n</i> -decane	10.3 ± 0.3	11 ± 2	Atkinson, 2003	6
<i>n</i> -nonane	11.0 ± 0.3	10 ± 2	Atkinson, 2003	9
<i>n</i> -octane	8.8 ± 0.3	8 ± 2	Atkinson, 2003	6
2-methylpentane	4.6 ± 0.3	5.2 ± 1.3	Atkinson, 2003	4
3-methylpentane	5.3 ± 0.3	5.2 ± 1.3	Atkinson, 2003	3
2,2,3-trimethylbutane	3.9 ± 0.3	3.8 ± 1.0	Atkinson, 2003	6
2-methylheptane	9.1 ± 0.3			0*
2-methylnonane	11.0 ± 0.3			0
Ethylcyclohexane	14.4 ± 0.3			0*

* Shaw et al. (2018) reported k_{OH} (323 K) for these compounds butane no literature k_{OH} value was found at 298 K.

Figures

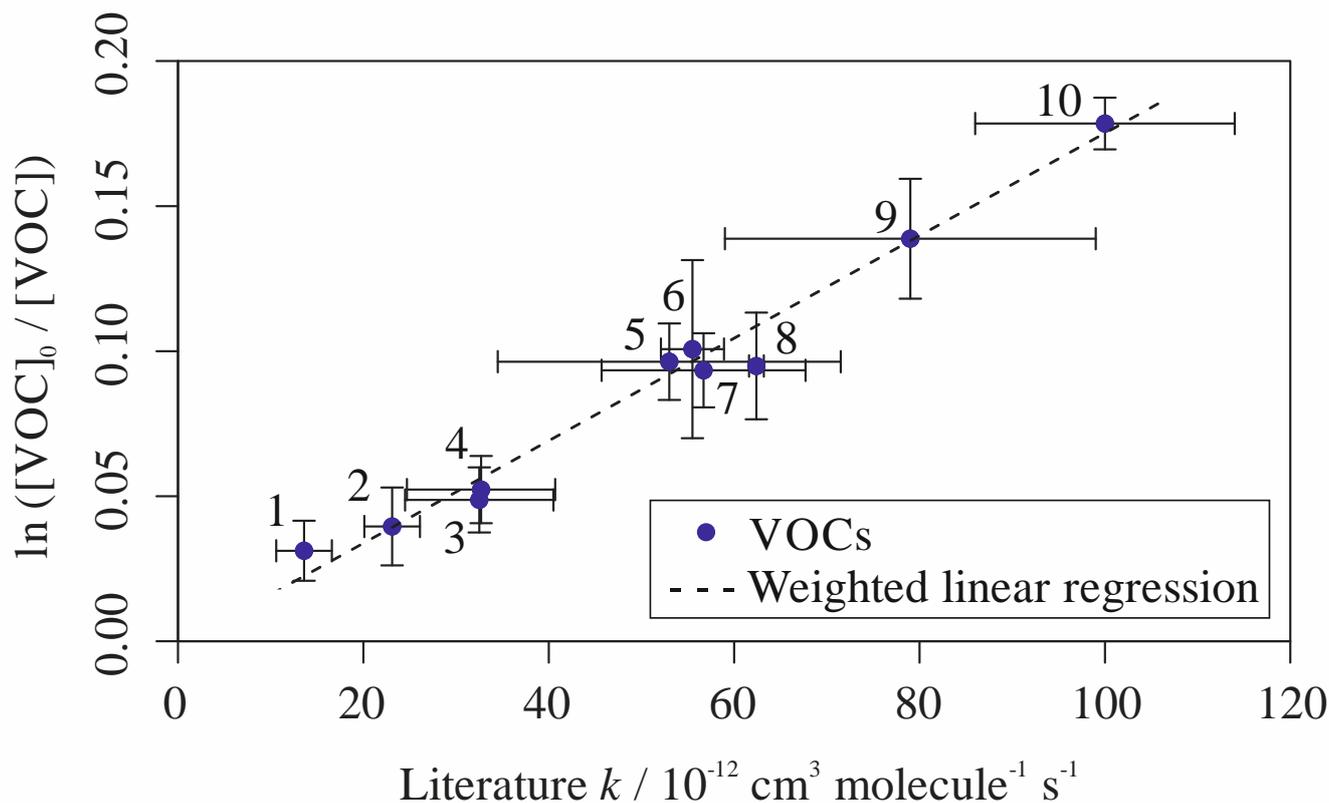


Figure 1: Relative rate plot for Mixture 1 (OH reactivity of 48 s^{-1}) in the absence of NO at $296 (\pm 2) \text{ K}$. Compounds with a reference rate coefficient for reaction with OH using evaluated literature values. Error bars on the y-axis, equal to 1 standard error, were calculated by combining the standard error in peak areas for eight lamp-off and eight lamp-on samples. Error bars on the x-axis were typically large (approximately $\pm 20\text{-}30\%$) and accounted for deviations from the predicted trend for all VOCs. A weighted (to the uncertainty in the y values) linear fit was used to generate the slope with $OH_{exp} = 1.8 (\pm 0.1) \times 10^9 \text{ molecules cm}^{-3} \text{ s}$ and $R^2 = 0.980$. The VOCs can be identified as follows: 1, *o*-xylene; 2, *m*-xylene; 3, 1,2,4-trimethylbenzene; 4, 1,2,3-trimethylbenzene; 5, α -pinene; 6, 1,2,4,5-tetramethylbenzene; 7, 1,3,5-trimethylbenzene; 8, 1,2,3,5-tetramethylbenzene; 9, β -pinene; 10, isoprene.

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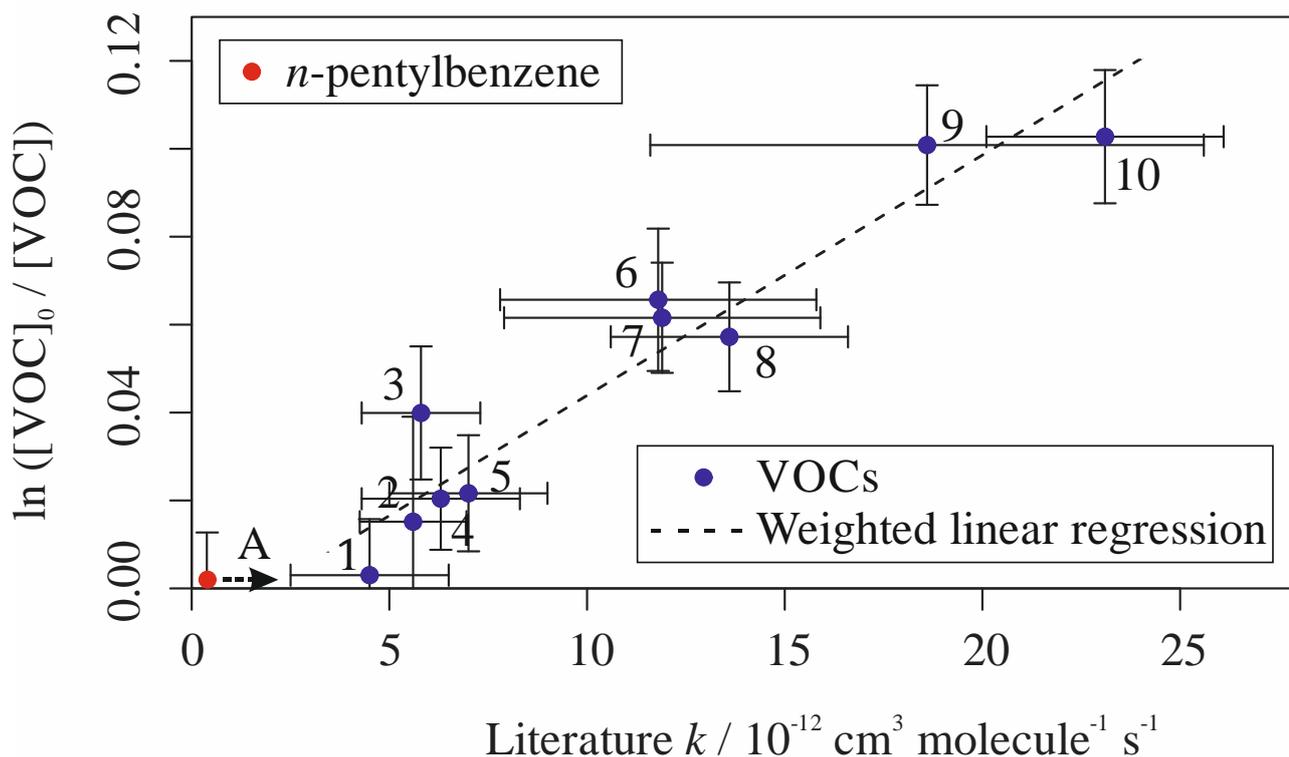


Figure 2: Relative rate plot for Mixture 2 (OH reactivity of 18 s^{-1}) in the absence of NO at $296 (\pm 2) \text{ K}$. Compounds with a reference rate coefficient for reaction with OH were plotted using evaluated literature values. Error bars on the y-axis, equal to 1 standard error, were calculated by combining the standard error in peak areas for six lamp-off and six lamp-on samples. Error bars on the x-axis were typically large (approximately $\pm 20\text{-}30\%$) and accounted for deviations from the predicted trend for most VOCs. A weighted (to the uncertainty in the y values) linear fit was used to generate the slope with $OH_{exp} = 5.5 (\pm 0.6) \times 10^9 \text{ molecules cm}^{-3} \text{ s}$ and $R^2 = 0.899$. Data for *n*-pentylbenzene (A) was not used in the calculation of OH_{exp} **but was included on the plot to illustrate its measured depletion factor**. The dashed arrow indicates that the k value for the target compound is determined by where it would fall on the measured OH_{exp} curve. The VOCs can be identified as follows: 1, *t*-butylbenzene; 2, toluene; 3, *n*-propylbenzene; 4, isopropylbenzene; 5, ethylbenzene; 6, 2-ethyltoluene; 7, 4-ethyltoluene; 8, *o*-xylene; 9, 3-ethyltoluene; 10, *m*-xylene. ~~The dashed arrow indicates that the k value for the target compound is determined by where it would fall on the measured OH_{exp} curve.~~

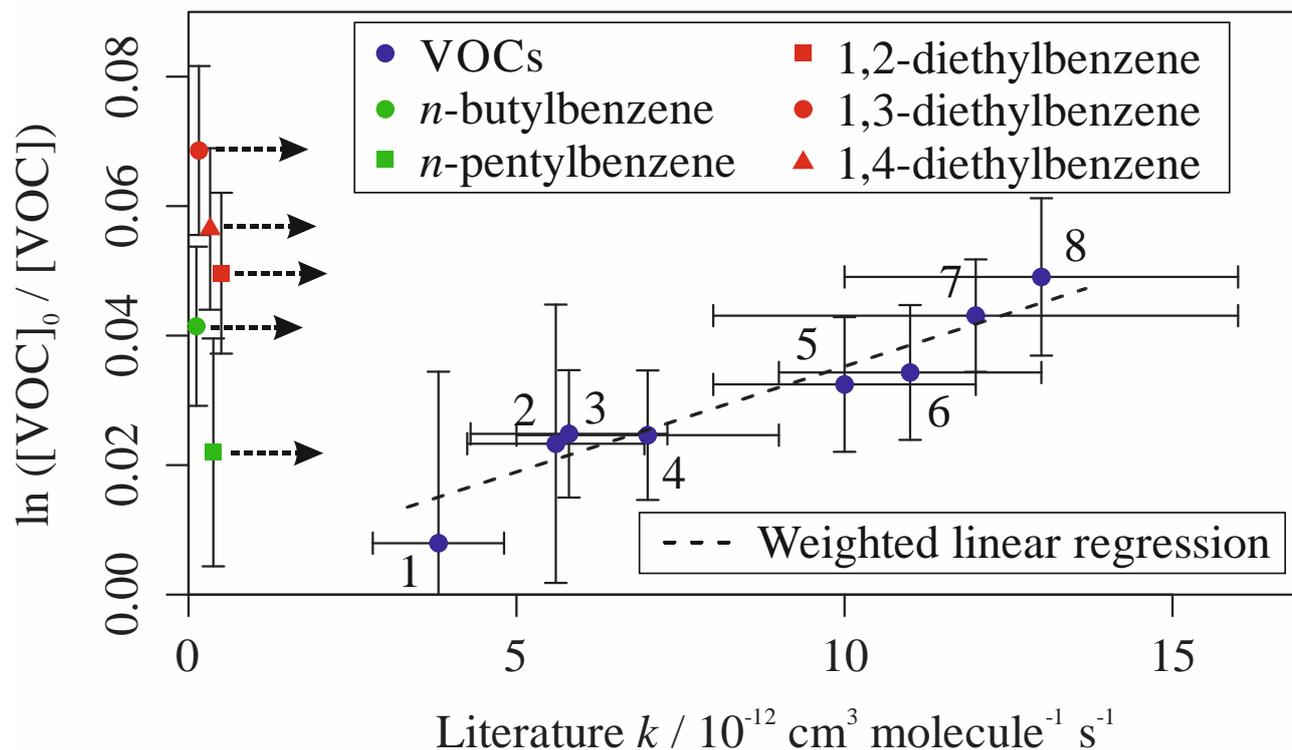


Figure 3: Relative rate plot for Mixture 3 (OH reactivity of 6 s^{-1}) and 40 ppb NO at $296 (\pm 2) \text{ K}$. Compounds with a reference rate coefficient for reaction with OH were plotted using evaluated literature values. Error bars on the y-axis, equal to 1 standard error, were calculated by combining the standard error in peak areas for eight lamp-off and eight lamp-on samples. Error bars on the x-axis were typically large (approximately $\pm 20\text{-}30\%$) and accounted for deviations from the predicted trend for most VOCs. A weighted (to the uncertainty in the y values) linear fit was used to generate the slope with $OH_{exp} = 3.3 (\pm 0.4) \times 10^9 \text{ molecules cm}^{-3} \text{ s}$ and $R^2 = 0.890$. Data for 1,2-, 1,3- and 1,4-diethylbenzene and *n*-butyl and *n*-pentylbenzene were not used in the calculation of OH_{exp} but were included on the plot to illustrate their measured depletion factors. The dashed arrows indicate that the k values for the target compounds are determined by where they would fall on the measured OH_{exp} curve. The VOCs can be identified as follows: 1, 2,2,2-trimethylbutane; 2, toluene; 3, *n*-propylbenzene; 4, ethylbenzene; 5, *n*-nonane; 6, *n*-decane; 7, 2-ethyltoluene; 8, *o*-xylene. The dashed arrows indicate that the k values for the target compounds are determined by where they would fall on the measured OH_{exp} curve.

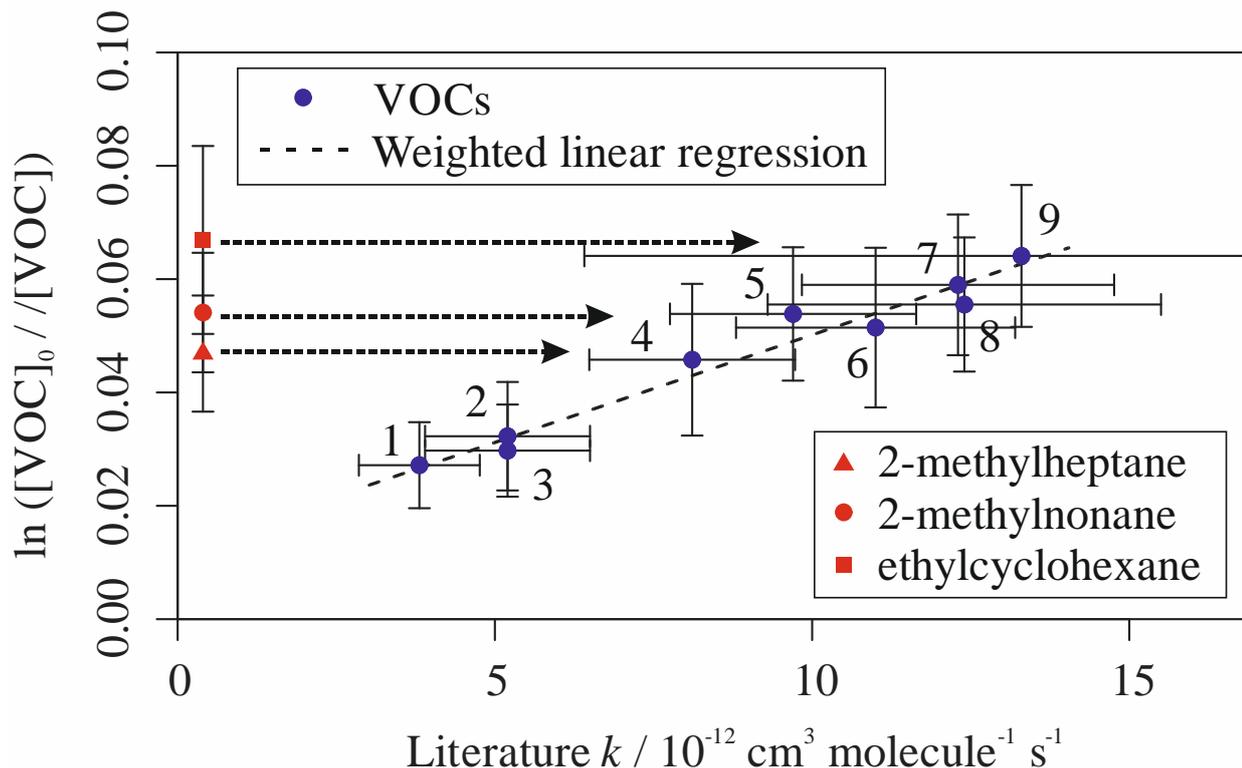


Figure 4: Relative rate plot for Mixture 4 (OH reactivity of 43 s^{-1}) and 50 ppb NO, at 296 K. Compounds with a reference rate coefficient for reaction with OH were plotted using their evaluated literature values. Errors on the y-axis, equal to one standard error, were calculated by combining the standard error in peak areas for six lamp-off and six lamp-on samples. Error bars on the x-axis were typically large and accounted for deviations from the line for all VOCs. A weighted (to the uncertainty in the y-values) linear fit was used to generate the slope, with a value of $OH_{exp} = 3.8 (\pm 0.2) \times 10^9 \text{ molecules cm}^{-3} \text{ s}$ and $R^2 = 0.971$. Data for 2-methylheptane, 2-methylnonane and ethylcyclohexane, which had no literature k (298 K) values, were not used in the calculation of the fit **but were included on the plot to illustrate their measured depletion factors.** The dashed arrows indicate that the k values for the target compounds are determined by where they would fall on the measured OH_{exp} curve. The VOCs can be identified as follows; 1) 2,2,3-trimethylbutane; 2) 2-methylpentane; 3) 3-methylpentane; 4) *n*-octane; 5) *n*-nonane; 6) *n*-decane; 7) *n*-undecane; 8) cycloheptane; 9) cyclooctane. ~~The dashed arrows indicate that the k values for the target compounds are determined by where they would fall on the measured OH_{exp} curve.~~

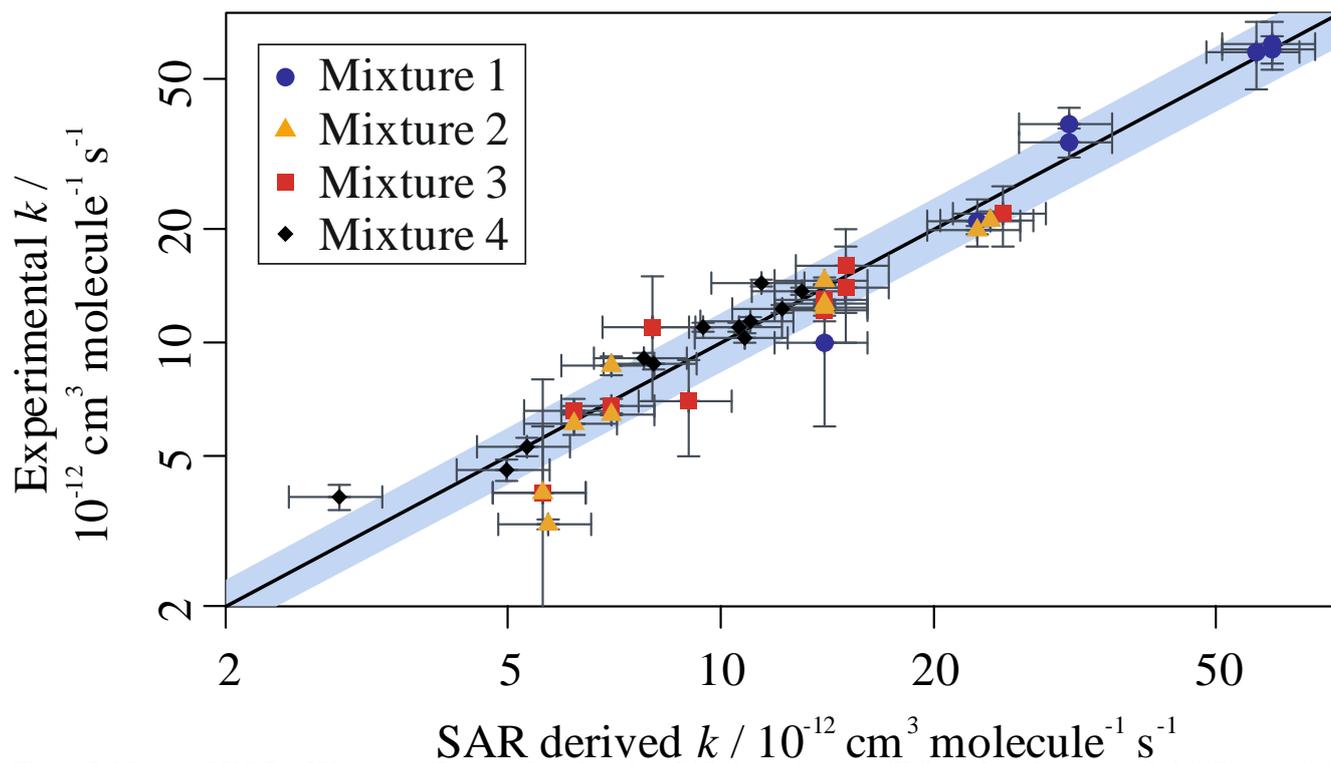


Figure 5: Measured VOC + OH rate coefficients plotted against SAR derived rate coefficients for all compounds in Mixtures 1, 2, 3 and 4. The grey shaded area demonstrates a 25% uncertainty in the 1:1 black gradient line. Most data fall well within this bound. The structure activity relationships used can be found in Jenkin et al. 2018a and Jenkin et al., 2018b. Outliers are; 2,2,3-trimethylbenzene, toluene, *t*-butylbenzene, *n*-butylbenzene, *n*-pentylbenzene and *o*-xylene. Most outliers have large derived uncertainties in their measured value.

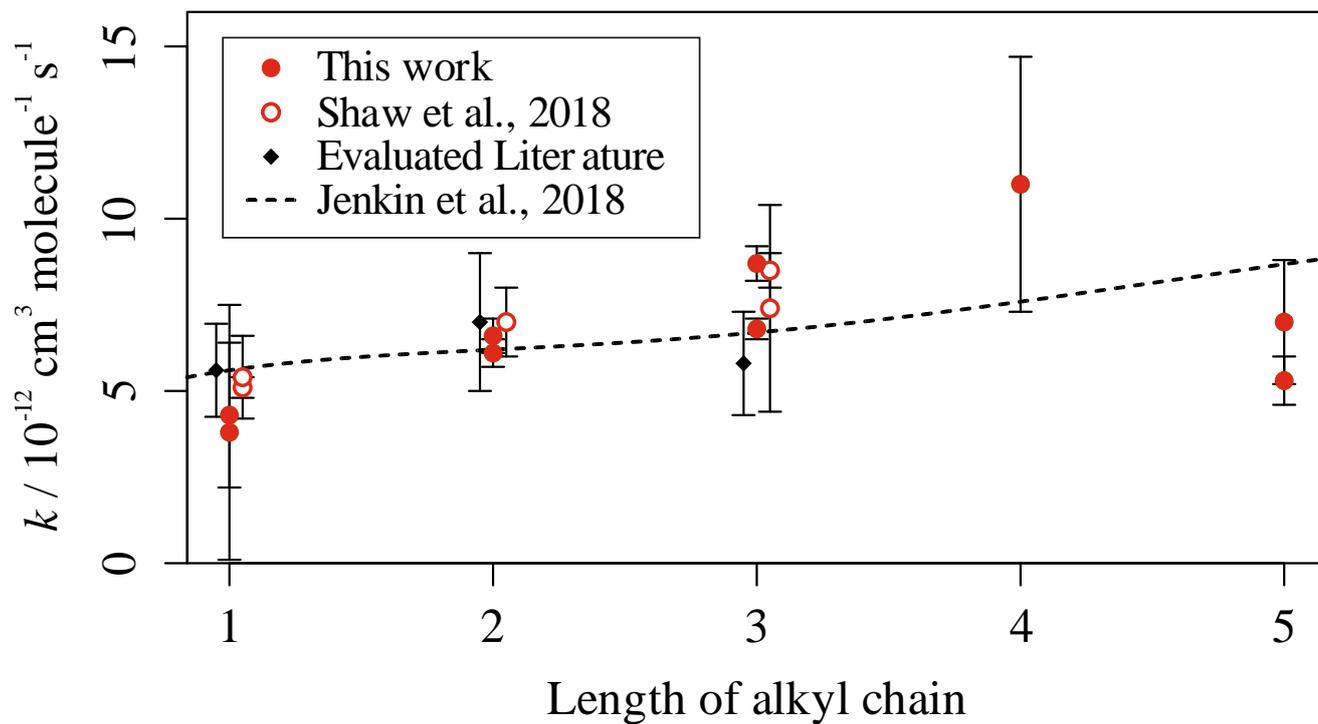


Figure 6. Experimentally derived (data points; see Table 2 and 3) and estimated SAR-derived (line; see Jenkin et al. (2018a)) k values for the reactions between OH and a homologous series of n -alkylbenzenes with different numbers of carbon atoms in the alkyl chain. Data from this, and other multivariate relative rate studies, are shown in red.

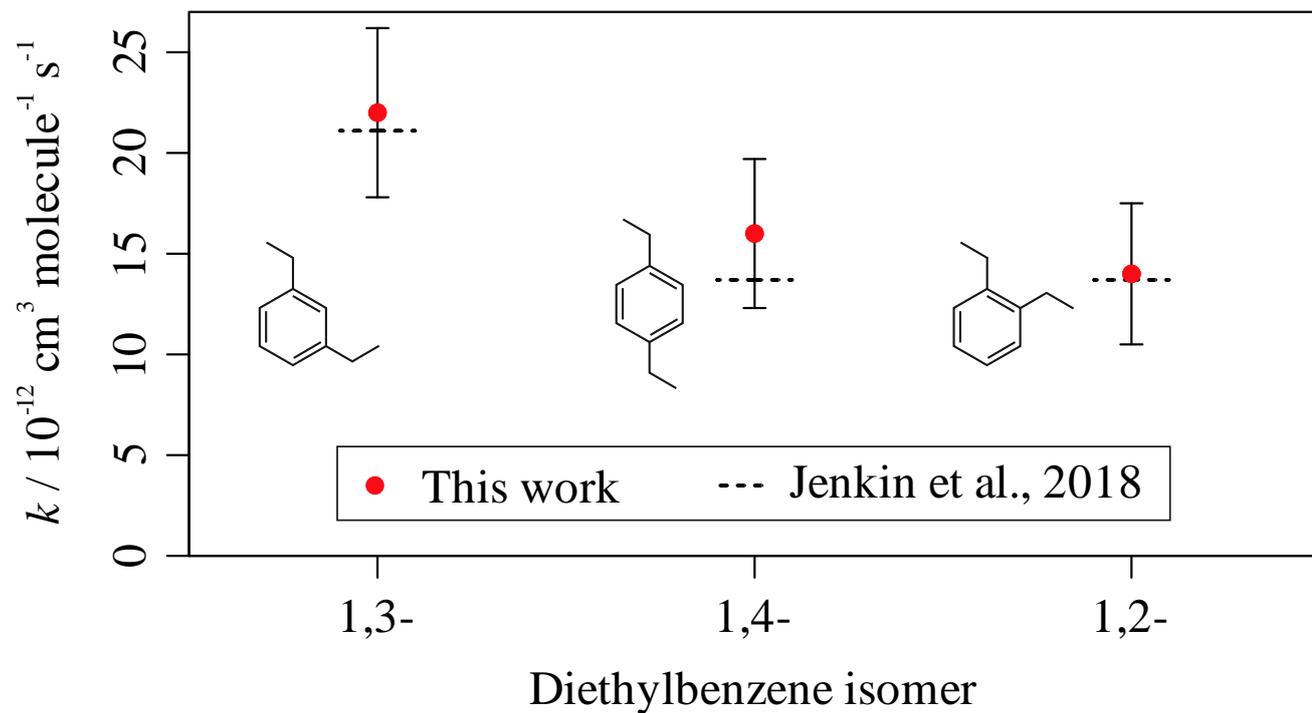
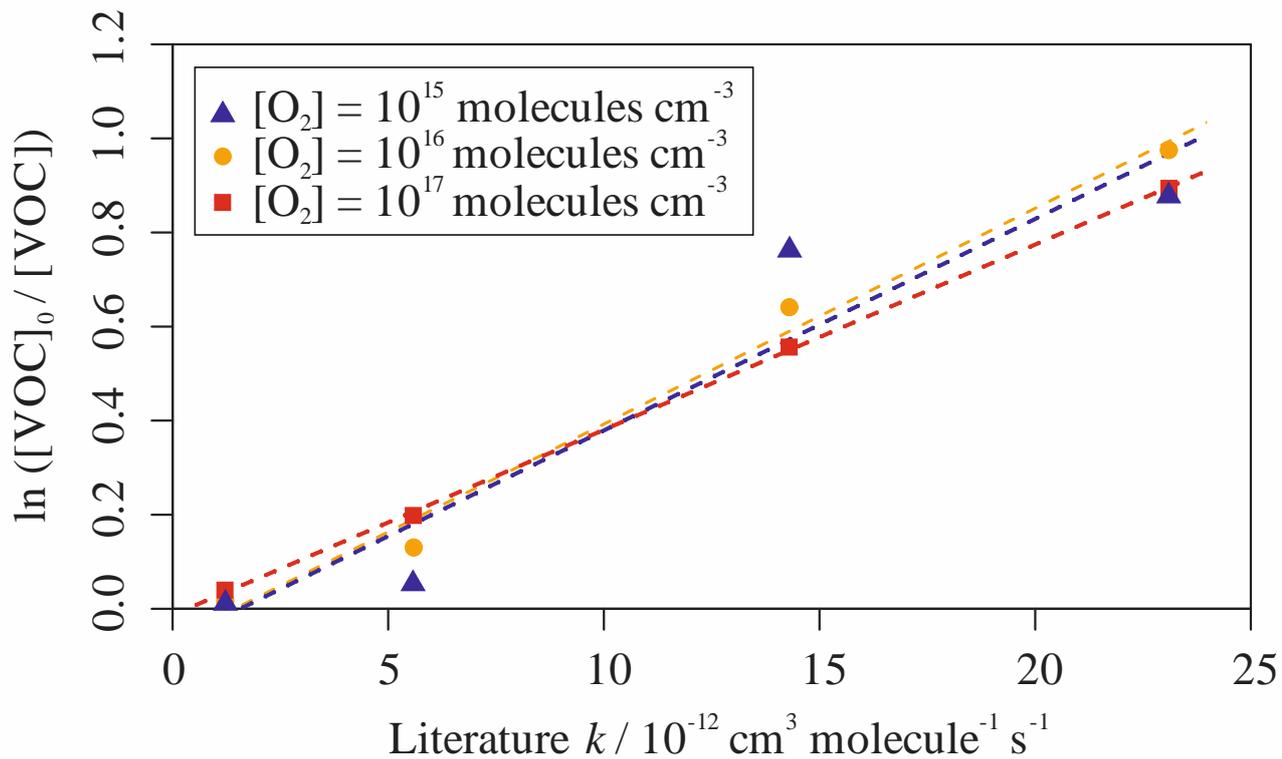


Figure 7. Experimentally derived (data points) and estimated SAR-derived (lines) k values for the reactions between OH and the three diethylbenzene isomers. Data from this work are shown in red.



5 **Figure 8.** Simulated relative rate plot for four aromatic VOCs when simulating different concentrations of O₂ in the reactor at 300 K. From left to right, the data points can be identified as; benzene, toluene, *p*-xylene and *m*-xylene. The R² values were 0.856, 0.981 and 1.00 for [O₂] = 10¹⁵, 10¹⁶ and 10¹⁷ molecules cm⁻³ respectively. The relationship between depletion factor and *k* value improved with increasing [O₂] suggesting that greater concentrations would be more likely to provide more accurate results.