Authors’ response to all referees for ACP-2017-917

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

Anonymous Referee #1

This is excellent work. I agree with the authors claim that this marriage of modern high-throughput analytical techniques with the well established and robust relative rate method represents a significant breakthrough in our ability to measure the kinetics of relevant atmospheric reactions. I look forward to this technique being used to substantially expand the atmospheric chemistry kinetic database, particularly at temperatures other than 298K.

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

Anonymous Referee #2

Shaw at al present a modified form of the relative rate method to derive self-consistent rate coefficients for reaction of OH with several VOCs simultaneously. The method is validated by comparison with a suite of OH-rate coefficients for various VOCs as found in compilations and evaluations of the kinetics literature.

The authors suggest that this method represents an improvement on the relative rate technique because of the higher throughput in terms of rate coefficients measured and also because of the multi-variate analysis, which does not rely on a single reference compound. I agree with the first statement, but would argue that the conventional relative rate method, with a single reference reactant also has advantages in terms of traceability (and thus simple future correction) of the rate coefficients obtained and also in the extension of the linear region over which the underlying kinetic framework works.

The authors agree with the referee’s comment that using a single reference reactant has advantages in traceability.

The manuscript has been updated to clarify this and now reads (P10L10): “*By using multiple reference compounds, the risk of a single erroneous reference value perturbing the rest of the data is reduced, assuming that all compounds behave in a similar way upon exposure to OH. This advantage does come at the expense of a loss in traceability. When changes are made to the reference rate coefficient for a specific measurement it is relatively easy to propagate the uncertainty change through to the relative rate measurements. When using multiple reference reactions, and generating a relationship between them, the transfer of an updated rate coefficient change would obviously be more complicated.*”

Although Shaw et al show that the rate coefficients are in good agreement with the literature their treatment of the non-linearity of the data (i.e. plots of ln(depletion factor) v k(literature)) is very weak and demands a more rigorous explanation.

A number of the referee’s comments concern the non-linearity of the data. Comments referring to this phenomenon are listed below, with the corresponding authors response in full below them. Comments referring to other aspects of the manuscript are addressed from page 5 onwards.

P6L1 “When using reactive gas mixtures containing VOCs which react rapidly with OH, a non-linear relationship between ln ([VOC]0[VOC]) and k may be observed, as compounds experience differing exposures to OH. Slow reacting VOCs may experience a larger exposure to OH relative to faster reacting VOCs.” This is the first time that this phenomenon is addressed in the manuscript and the explanation is not helpful. In a mixture of reactive *gases, the number of OH reactions (integrated over time) of any single VOC will depend on the (time dependent) steady state OH concentration, which itself depends on the overall reactivity and its production rate. Slow reacting VOCs will be less depleted than fast reacting VOCs, but the relative change should still be defined by the relative rate coefficient.*

P9L17 "4. Whilst this is inconsistent with Eq. (3), it does not necessarily detract from the relative rate nature of the experiment as a reliable and consistent function can still be plotted through the data. This type of distribution possibly occurs when gas mixtures contain low concentrations of very fast reacting VOCs and arises due to poor mixing conditions within the reactor." I find this aspect of the work needs more attention. The plot is in fact linear up to a depletion of reactants of 35-40 % and in this regard is completely compatible with the data shown in Figure 3. The curvature occurs at large depletion. Would curvature be apparent at a reactivity of 240 /s if there were more time for reaction or more OH available (to increase the depletion factors) ? The authors rather hand-waving explanation about mixing needs to be more rigorously discussed as this might represent a limitation of this method. Note that similar (non-linear) effects were reported by Sinha et al in their paper on the comparative reactivity method, which was found to be dependent on the reactivity of the system and which could be explained (via numerical simulation) as arising from a departure from first-order kinetics. Perhaps simulations could shed some light on these effects here too ?

P10L19 "Figure 5 shows an example relative rate plot for Mixture 2; for which a linear relationship is observed across all OH reactivities tested". As for Figures 3 (non-zero intercept) and 4 (very obvious curvature at large depletion factors), the data do not lie on a straight line but on a curve. This is the reason for the large intercept. The data cover depletions of between 13 % and 25 % only and a straight line fit will of course go through the data points in this small range. The question that needs to be addressed here is why the intercept (at a rate constant of zero) indicates large depletion still.

P11L4 "Likely due to the small concentrations of VOCs injected and the large range in VOC + OH rate coefficients" is not an explanation of the phenomenon. The nonlinearity in these plots requires more rigorous examination.

The referee is correct, significant curvature occurs at depletions larger than 40 %, with most plots being linear up to a depletion factor of approximately 0.4. Up to this point, rate coefficient estimations made using either the curved relationship or linear regression are in good agreement, within errors (see Table 3). It is currently not possible to experimentally determine what the impact of a larger initial [OH] would be at higher OH reactivity.

Model simulations have been performed to try and understand the reason behind the observed deviation from linearity. The simulations were conducted using Kintecus and incorporated the OH + VOC reactions for Mixture 1, as well as very simple HO_x chemistry ($OH + OH \rightarrow H_2O + O$, $k = 1.48 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; $OH + OH \rightarrow H_2O_2$, $k = 6.20 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; $OH + HO_2 \rightarrow H_2O + O_2$, $k = 1.10 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, $k = 1.60 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}).

To simulate incomplete mixing of OH, the reactor was divided into three distinct theoretical air parcels; one where ⅓ of the [VOC] is exposed to a low [OH], one where ⅓ [VOC] is subjected to a high [OH] and one where ⅓ [VOC] is exposed to a level of [OH] between these two high and low values. The depletion factors of the VOCs in each of these air parcels can be plotted separately, or summed together to yield an average depletion factor. The average depletion factor is more representative of what is actually measured by the GC-MS, assuming that thorough mixing of all air parcels takes place after the reactions with OH have occurred.

Figure S1 shows that in each of these air parcels, the VOCs are depleted relative to their rate coefficients. The adjusted R^2 values for each of the three linear regressions is 1.0.

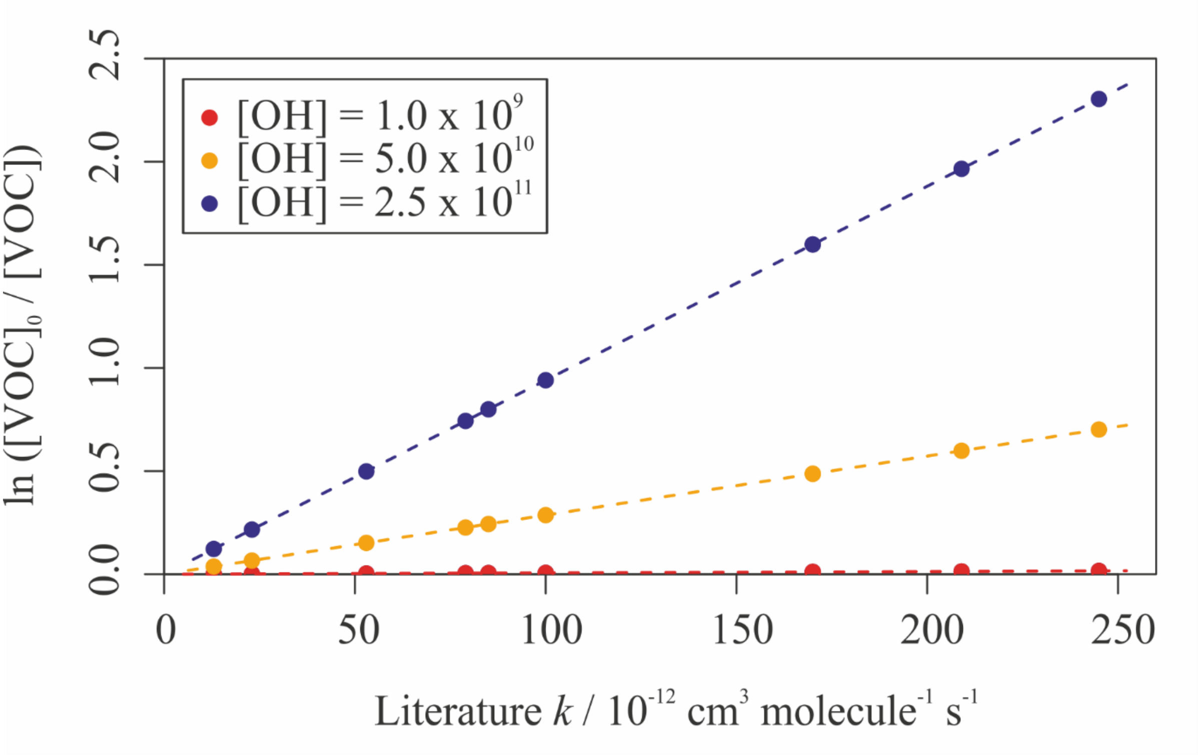

Figure S1. Simulated depletion factors for Mixture 1 (OH reactivity = 50 s^{-1}) plotted against literature rate coefficients. Here three air parcels are simulated separately, with each air parcel containing ⅓ [VOC] and exposed to different [OH] (molecules cm^{-3}).

However, if the concentrations in each section of the reactor are summed before the depletion factor is calculated, as happens prior to sampling by the GC-MS, the resulting plot against rate coefficient is indeed curved, as shown in Fig. S2.

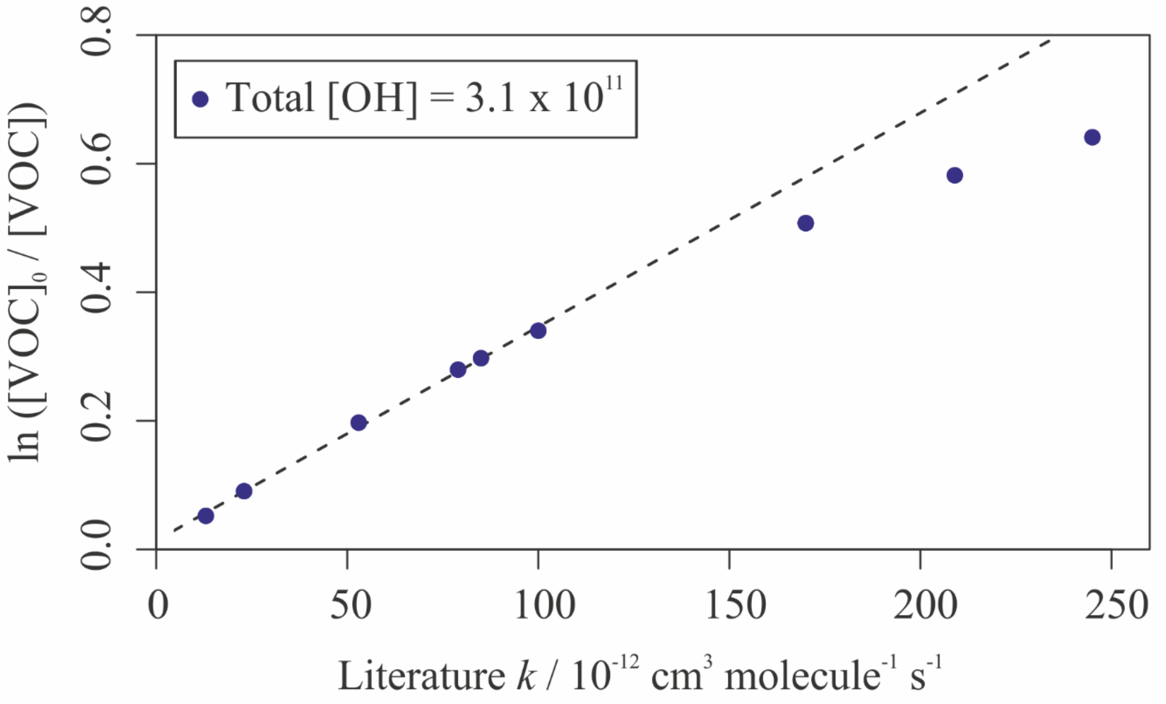

Figure S2. Simulated depletion factors for Mixture 1 (OH reactivity = 50 s^{-1}) plotted against literature rate coefficients. Here the concentrations of the VOCs in each of the three simulated air parcels (Fig. S1) are summed and the depletion factor for the final concentration is plotted against literature rate coefficient.

This curvature still occurs at higher [VOC], but is much less pronounced, to the extent that the relationship can be assumed to be linear. Figure S3 shows the same simulation for a [VOC] of 10 ppb, or OH reactivity of 290 s^{-1}. Note that the model reproduces the discrepancy in depletion factor observed experimentally and that the curvature is only really noticeable when the depletion factor is greater than 0.4.

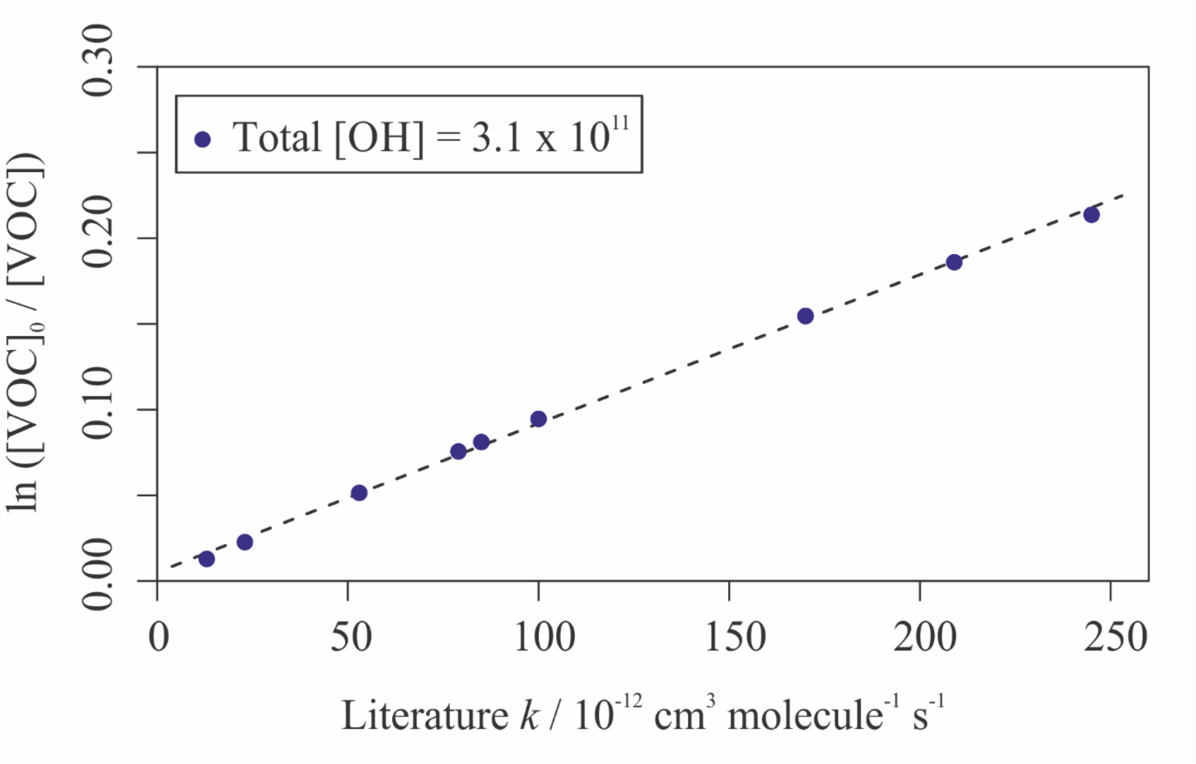

Figure S3. Simulated depletion factors for Mixture 1 (OH reactivity = 290 s^{-1}) plotted against literature rate coefficients. Here the concentrations of the VOCs in each of the three simulated air parcels are summed and the depletion factor for the final concentration is plotted against literature rate coefficient.

Whilst this artefact of the experiment does represent a limitation, at least in terms of sensitivity towards measuring rate coefficients towards the greater end of the reactivity spectrum, it does not affect measurements made for VOCs with a depletion factor less than 0.4. As mentioned before, if a consistent function can be plotted through the data and an unknown is interpolated using that function, the relative rate conditions should still apply.

This model analysis, explaining the observed curvature, has been added to the Supplementary Information in a section titled 'Kinetics simulations of poor mixing resulting in non-linearity'.

The authors should address the following points in a revised manuscript:

P3L10 "Thus, this aspect of gas-phase kinetics represents a fundamental pillar of atmospheric and, more widely, environmental science." The importance of kinetics, and laboratory studies as a whole, has been recently highlighted by Burkholder et al.(J., Env. Sci. Tech., 51, 2519-2528, 2017) which could be cited here.

Citation added.

P3L17 replace "such as rate coefficient" with "such as the rate coefficient"

Amended to "*parameters such as the rate coefficient…*".

P3L18 replace "method" with "semi-empirical method"

Amended to "*thereby providing a semi-empirical method…*"

P3L29 replace "which ideally react at a similar rate" with "which ideally has a similar rate coefficient"

Amended to "*which ideally possess similar rate coefficients…*".

P3L30 replace "the ratio of their depletion allows" with "the ratio of their depletion factors (or fractional depletion) allows"

Please refer to comment P5L23.

P4L25 "Rather than rely on one reference VOC, a subset of the existing OH + VOC kinetic database is used to place the experimental relative rate data on an absolute scale, thereby reducing uncertainties." I do not completely agree. The uncertainty will depend ultimately on the quality of the literature data for several trace gases and depend sensitively on how the real uncertainties in each of these literature rate coefficients are 1) assessed and 2) how they are used (weighting) in the fitting procedure. I do not think that a singly measured rate coefficient compared to one (or two) well known reference reactants in separate experiments is less accurate. It might take more time (per VOC), but it will be more reliable.

The authors agree that the use of multiple reference reactions does not reduce uncertainties but rather reduces the reliance on single reference reactions. The manuscript now reads "*A subset of the existing OH + VOC kinetic database is used to place the experimental relative rate data on an absolute scale, thereby reducing the reliance on a single reference reaction.*"

P4L30 "near ambient" ?. VOC oxidation in the atmosphere occurs over a wide range of temperatures and pressures. Perhaps "ambient" is the wrong term here as conditions of one bar and 295-323 K represent only a small fraction of the atmosphere.

Amended to "*Experiments were conducted under conditions of 1 bar (N_2) and 298-323 K…*" to clarify the reactor conditions.

P5L23 "depletion" Perhaps fractional loss of a VOC ?

'Depletion' is not an adequate term to describe the parameter here. Any equivalent mentions of 'depletion' within the manuscript have therefore been amended to 'depletion factor' to aid in clarification. Depletion factor refers specifically to the parameter $\ln\left(\frac{[\mathrm{VOC}]_0}{[\mathrm{VOC}]}\right)$, described on P5L24 in Eq. (3), and not to a depletion in terms of concentration.

P5L31 "despite the establishment of laminar flow". "Because of laminar flow rather than despite laminar flow ? Laminar flow at atmospheric pressure reduces mixing. Turbulent flow forces mixing. Is the flow really laminar ? Give the Reynolds number and entrance length for acquiring laminar flow.

To clarify with regards to the Reynolds number (R_e): the initial flow of humidified N_2 (2000 sccm) has Re = 88 with an entrance length of 0.1 m. The flow after injection of the VOC mixture (total of 3000 sccm) has Re = 132 and an entrance length of 0.2 m. The low values for Re suggests that laminar flow is established within the reactor, both initially and after injection of the VOCs. However, these calculations do not take into account that the VOC mixture is injected perpendicular to the main flow, which is likely to cause considerable turbulence and facilitate mixing.

The manuscript text has been amended to read "*However, because of the establishment of laminar flow in the reactor, thorough and complete mixing of OH is unlikely to take place before the reactions with VOCs occur (see Supplementary Information).*" A section 'On the establishment of laminar flow' has been added to the Supplementary Information to support the text in the manuscript.

P6L10 " . . . the use of multiple known k values should minimise any systematic error induced compared with using a single reference compound." This statement is too broad. Systematic error will depend on how well known the reference rate coefficients are and how close they are (in depletion factors) to the unknown VOC. i.e. a reference VOC with a rate coefficient that is a factor 10 faster and which has a large associated uncertainty will not improve the accuracy of the k derived.

The authors agree that this must be clarified further. The text has been amended to "*the use of multiple known k values should reduce the reliance on any single reference reaction*".

P7L1 Perhaps worth mentioning the implicit assumption that trace gases are not selectively lost in the trapping (reaction with condensed water) or desorption process (via thermal decomposition).

The authors respectfully disagree that this is a necessary implicit assumption for the GC sampling in this work. Due to this method relying on the relative change in the concentration of VOCs from "lamp off" to "lamp on" samples, so long as the sampling is consistent for the two situations, it should not matter. If a trace gas *is* selectively lost during sampling this will not affect the results if the loss is consistent from "lamp off" to "lamp on".

The text (P5L22) has been amended to "*Assuming consistent trapping and sampling with both the lamp switched off and the lamp switched on, the depletion of an individual VOC, with a known OH rate coefficient can be evaluated using simple kinetic equations.*" to aid in clarification of this.

P8L4 How was the total OH reactivity estimated if one compound did not have a rate coefficient prior to conducting the experiments ?

The total OH reactivity is not a parameter necessary for the calculation of *k* values in the paper. The authors thought it useful to include in order to distinguish between differences in mixtures, especially to differentiate between a single mixture that was studied under different flow regimes.

To make this clear, the text (P7L23) has been amended to include the sentence "*This parameter is not necessary for the measurement of k values but is provided in order to differentiate between separate mixtures and also between the same mixture studied under different flow regimes.*"

Regardless, the OH reactivity of a mixture containing an unknown can be estimated in a number of ways, for example, by using a SAR in the absence of experimental *k* values.

P9L14 "However, despite the intercept being close to zero, linear fits with a non-zero intercept were found to be a more appropriate approximation" This is a wishy-washy statement. How is "more appropriate" defined and why ?

'More appropriate' refers to the fit being more precise within the range of OH + VOC *k* values, as we are not concerned with extrapolating to 0 – or indeed outside the range of OH + VOC *k* values. Whilst this is referred to at P6L12, the text at P9L17 has been clarified to read "*However, despite the intercept being close to zero, linear fits with a non-zero intercept were found to be a more appropriate approximation across the range of k values studied. Extrapolation beyond the range of reference OH + VOC* k *values is not necessary to make accurate measurements of* k *values.*"

Adjustments to Figures 3-5 have been made to reflect this – the linear fit has been restricted to only the range of OH + VOC reactions measured, highlighting that knowledge of the intercept is not necessary.

P9L15 Replace "needs to only be a. . ." with "needs only to be a. . ."

Amended to "*there needs only to be a…*".

P9L16 "a three-parameter exponential distribution function, given in Eq. (5) was used to fit the data. . ." How was this function chosen ? Would it not make more sense to select a function that goes through zero depletion when k_literature is zero. This becomes more apparent when you examine Figure 7.

This function was the only function which consistently and reliably produced a fit to the data. Many other functions could not be resolved using the Origin software for one or more sets of data. The authors agree that the chosen function is not perfect but in the absence of any other, necessitates its use. The authors would like to reiterate their opinion that there needs only be a consistent function that can model the observed data well for the relative rate concept to hold true.

P9L24 "The gradient of the line in Fig. 3 is equal to the integral of OH concentration over time." This can also be calculated from the OH concentration, derived from the depletion rate of a single VOC and the flow parameters of the reactor. The authors should compare this. It would in any case be interesting to read what the production rate of primary OH is and what OH levels are present.

An estimate of the [OH] in the reactor may be made by totalling the losses in each VOC, assuming their initial concentrations have been estimated to a reasonable degree. This is likely to produce an underestimation of the [OH] generated by photolysis (due to anticipated losses of OH to HO_2, a by-product of H_2O photolysis) but may indicate [OH] availability immediately prior to the injection of VOCs. For Mixture 1, summing the losses in the VOCs, results in an average [OH] = 1.6 (± 0.5) × 10^{11} molecules cm^{-3} over the different OH reactivities tested. For the Mixture 2, the average [OH] = 0.9 (± 0.2) × 10^{11} molecules cm^{-3}.

Further insight may be gained using a kinetic model to estimate the extent of OH losses to HO_2. Using depletion as a diagnostic, the kinetic model is best matched to experimental results using [OH] = 3.1 (± 1.0) × 10^{11} molecules cm^{-3} for the monoterpenes mixture and [OH] = 1.3 (± 0.2) × 10^{11} molecules cm^{-3} for the alkenes mixture.

These values are of a similar order of magnitude with that calculated for a similar system, in which the reaction of OH with methanol was used to estimate the [OH] produced in the reactor, via the concentration of formaldehyde detected. This was measured to be approximately 2.6 (± 1.5) × 10^{10} molecule cm^{-3} (Cryer, 2016).

P9L26 "Li et al. (2015) and Peng et al. (2015) found that increasing the OH reactivity results in an increased rate of removal of OH radicals from the system." I don't understand this statement. Increasing the OH reactivity *must always increase the rate of removal of OH (which, at any point in time, is [OH]*reactivity). Are the authors indicating that changes in the recycling of OH may occur for systems with more highly reactive hydrocarbons or is this a manifestation of secondary reactions of OH with the products formed (which may be more or less reactive that the initial mixture) ?*

This section is confusing due to the cyclical nature of arguments. The explanation of OH exposure decreasing with increasing OH reactivity isn’t necessary and was therefore removed from the manuscript.

P9L29 “Using Eq. (3) it is possible to estimate new k values at room temperature (295 (± 2) K) for all components in Mixture 1. . .” Then the equation must be modified as it presently only deals with isoprene reacting with OH. As the depletion factor for isoprene (data point at 100e-12) has the lowest associated uncertainty in Fig 3, the weighted fit is forced to pivot through this data point. I would like to see the uncertainty in the literature k on this plot (and on Figs 4-7) and also read more about the assessment of uncertainty and the weighting procedure used in the fit (which presumably took errors in both the x and y directions into account).

The authors agree that the referral to Eq. (3) here, which specifically mentions isoprene, is confusing. In order to clarify that a general expression should be used, which is similar in form to Eq. (3) and derived from the weighted linear regression (i.e. taking into account the non-zero intercept), the text was amended to “*By referring to a generalised version of Eq. (3), and using the function of the weighted linear regression, it is possible to estimate new* k *values at room temperature…*”.

To make the plots more readable, I suggest labelling each data point with the VOC concerned, otherwise one has to refer to the tables with the literature rate coefficients to see which data point is which VOC.

Please refer to the comments on Figs. 3-5 and 7.

P10L1 “The majority of VOCs. . .. .” Here we are dealing with the advantages over the conventional relative rate approach. Many rate coefficients in the literature have been derived using relative rate methods and a certain set of "common" reference reactants chosen because they have well defined rate constants. For any particular pair of reactants, the uncertainty of the rate constant derived by the relative rate method is lowest when reference and reactant have similar rate coefficients. One could argue that mixing in reactants that react much more slowly (or quickly) actually reduces the accuracy. Also, unlike in the conventional relative rate method, where changes (i.e. improvements over time) in the rate constant for a reference reactant can be transferred easily to correct all values obtained for other gases measured relative to it, the relationship in the multivariate case is more obscure.

The use of multiple rate coefficients does have drawbacks in the traceability of measurements, should adjustments to recommended values be made. However, the authors would argue that using a range of multiple reference VOCs, some which react more slowly and some more quickly, gives an advantage in terms of reliability, in that the measurements no longer rely on a single value.

The manuscript has been updated to clarify this and now reads (P10L10): “*By using multiple reference compounds, the risk of a single erroneous reference value perturbing the rest of the data is reduced, assuming that all compounds behave in a similar way upon exposure to OH. This advantage does come at the expense of a loss in traceability; when changes are made to the reference rate coefficient for a specific measurement it is relatively easy to propagate the uncertainty change through to the relative rate measurements. When using multiple reference reactions, and generating a relationship between them, the transfer of an updated rate coefficient change would obviously be more complicated.*”

P10L8 Replace “measurements” with “rate coefficient measurements”

Amended to "*the wider literature contains rate coefficient measurements…*".

P10L12 Are the Hites et al measurements relative or absolute ? Delete the comma after "rate"

Amended and included the word 'relative'. The text now reads "*Recent relative rate measurements of the OH + myrcene reaction by Hites and Turner (2009) and Kim et al. (2011)…*".

P10L14 Replace "limonene oxidation rate . . ." with "the rate coefficient for reaction of limonene with OH . . ."

Amended to "*Our measurement of the rate coefficient for the reaction of limonene with OH…*".

P10L16 Replace "value" with "rate coefficient"

Amended to "*The measured rate coefficient for the OH +* o-xylene *reaction…*".

P10L17 "this is an erroneous measurement that arose due to the OH initiated depletion of o-xylene being too small and subject to large relative errors". Not sure about this explanation. A seven percent change should be sufficient to get within about 20-30 % of the true number. A factor 10 disagreement must have a different origin.

An anomaly in the calculation of error propagation resulted in this discrepancy. This has since been corrected and the value for *o*-xylene adjusted to 4.8 (± 7) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. This is more in line, within error, with the recommended rate coefficient of 13 (± 3) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. However, the large errors on the measured value are still likely due to *o*-xylene lying at the extremes of the reactivity of Mixture 1. Minor adjustments were also made to some other rate coefficients in Mixtures 1 and 2 owing to the same anomaly (12 of the 21 measurements were changed. Of these 12, 9 were adjusted by less than 3 % with *o*-xylene and 1-hexene having adjustments of 67 and 37 % respectively. Note that both these compounds were at the lower extremes of their respective mixtures.)

The manuscript has been amended to "*The measured rate coefficient for the OH +* o-xylene *reaction, of 4.8 (± 7) ×* 10^{-12} cm^3 $molecule^{-1}$ s^{-1} *is the only result which is not totally consistent with the literature. It is likely that this anomaly arose due to* o-xylene *being at the lower extreme of the mixture reactivity.*"

P11L1 "order to prevent excessive partitioning of the less-volatile. . . ..." Be more precise. what is excessive in this context ? what might be the effect of partitioning to the walls in terms of its impact on the relative concentration changes after reaction ?

The wording here is ambiguous: 'excessive' in this context refers to losses which would lower the concentration below the limit of detection for the analytical method. Partitioning to the walls, so long as consistent between lamp off and lamp on samples, should not impact the relative concentration changes. The manuscript was amended to "*in order to avoid greater uncertainties as a result of partitioning of the less-volatile VOCs to the reactor surfaces.*"

P11L9 The value obtained for myrcene is actually (within combined uncertainty) in agreement with the literature value listed.

This is correct and the manuscript has been updated accordingly: "One measurement stands out as contrasting with its literature value; that for β-ocimene, of 950 (± 800) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}."

P11L19 report the gradient along with its standard deviation.

Amended to "*The gradient of this regression is 1.0 (± 0.02)…*".

P11L26 "Whilst there is still a good correlation between . . ." Does the "good correlation" refer to the fact that the "non-linearity" can be removed by a fitting function ? In this case, any data that can be fitted with a function (no matter how complex) could be described as well correlated. This tends to disguise the fact that the relationship between the depletion factors and k_literature is not entirely understood.

Amended to "*Whilst there is still a correlation between* $ln\left(\frac{[VOC]_0}{[VOC]}\right)$ *and* k…".

P12L30 OH + aromatics. To what extent do these reactions involve reversible addition of OH to the aromatic ring, which can then react with O2 (or not in this case as the experiments are in N2). Can the lack of O2 alter the effective (forward) rate coefficient ?

The lifetime of the OH-aromatic adducts formed by addition of OH to the aromatic ring is approximately 0.3 s at 298 K (Atkinson and Arey, 2003). This lifetime decreases rapidly with increasing temperature. Whilst our experiments are conducted in N_2, we estimate that O_2 is present in the reactor on the order of 10^{16} molecules cm^3 due to the use of ambient air to prepare Mixture 3 and impurities in the N_2 gas. The reaction between OH-aromatic adducts and O_2 is expected to proceed at between 2-8 × 10^{-16} cm^3 $molecule^{-1}$ s^{-1} for the OH-benzene, OH-toluene and OH-xylene adducts (Atkinson and Arey, 2003). The lifetime of the OH-aromatic adducts, with respect to O_2, is therefore likely to be much less than 1 s. For this reason, we anticipate that most of the OH-aromatic adducts do not undergo thermal decomposition to the original aromatic species and OH, and instead react with O_2. This is supported by rudimentary kinetic models*, where < 10% of the OH-aromatic adducts undergo thermal decomposition.

This, and other issues concerning OH + aromatic reactions, will be discussed in a future publication focusing on OH + aromatic relative rate measurements.

* Kinetic simulations performed in Kintecus incorporating all aromatic species in Mixture 3. The model included reactions between aromatics and OH forming an OH-aromatic adduct product. This product could then react with O_2 with an estimated rate coefficient of 6 × 10^{-16} cm^3 $molecule^{-1}$ s^{-1} or decay back to the original aromatic species and OH, with an estimated rate coefficient of 2 s^{-1}.

P13L3 "and can only include compounds for which authentic standards or pure raw materials are available." Why pure ? An impure sample will work perfectly well as long as it can be selectively detected. This is the main advantage of relative rate versus absolute methods.

The purity of the compound is not necessary here: the word "pure" has been removed from the manuscript.

P13L14 "There is also likely to be a large variety in the concentrations at which atmospheric VOCs exist". I think this is proven rather than "likely".

Amended to "*Atmospheric VOCs exist at a large range of concentrations…*".

P13L15 "which could have an adverse effect on the uniformity of individual VOC exposure to OH" What is the "adverse effect" and what does "uniformity of exposure to OH" mean ?

This sentence has been removed from the manuscript. Whilst the range in VOC concentrations in the atmosphere does represent a practical challenge in real air sampling, it is by no means the most significant.

P14L15 "OH. However, a significant section of the plot lacks literature data for comparison" In this case it would be beneficial to spike the air with a few reference gases with well-known rate coefficients before entering the reactor.

The authors agree that, in hindsight, spiking the air with reference compounds would have been beneficial, had we known there would be a considerable gap. However, three of the four monoterpenes would have fit into the aforementioned gap, had they not been depleted to below the limit of detection. A sentence has been added to the manuscript suggesting this: "*It may therefore be beneficial, in future work deriving rate coefficients from real air samples, to synthetically spike the air with a range of reference compounds whose rate coefficients are accurately known, in order to ensure that the best possible correlation between depletion and literature rate coefficient can be generated across the desired range.*"

P15L13 "this method can produce novel results. . ." perhaps "can produce rate coefficients for VOCs, the OH-kinetics of which have not been investigated to date" or similar.

Amended to "*We have shown this method can produce rate coefficients for VOCs, the OH-kinetics of which have not been investigated to date…*".

Figures

Figures 3-5 and 7 should be improved by 1) adding the error bars representing the uncertainty in k. I consider this to be very important in order to assess the quality of the data. 2) identifying the VOCs.

Identifying the VOCs on the plots would improve readers' understanding and interpretation. Figures 3-5 and 7 have therefore been amended, with the data points numbered with their corresponding identity included as part of the figure captions.

Whilst including x-axis (*k* value) uncertainties does aid in comprehension of the linear fit, the authors believe that some of the resultant plots are exceptionally cluttered (see example below). For this reason, plots including the x-axis uncertainties for Mixture 2 will be included as part of the Supplementary Information, whilst the cleaner plot for Mixture 2 remains as part of the main manuscript.

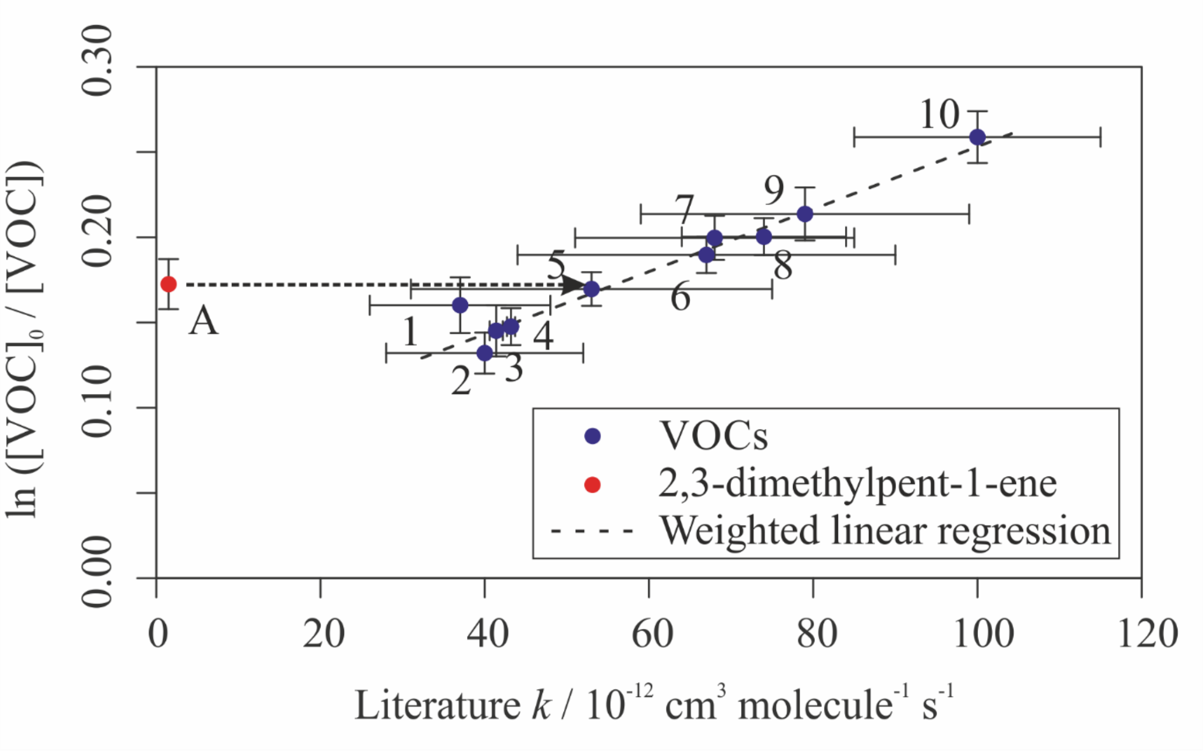

Figure 7: The inset obscures a large part of the x-axis of the main plot. This can be done better

The authors agree that the inset is not necessary and it has therefore been removed.

Anonymous Referee #3

This manuscript describes flow tube studies in which OH radicals are reacted with a mixture of volatile organic compounds (N>10) simultaneously, in order to generate a self-consistent set of reaction rate coefficients. The concept for the experiment is good, but I question the generality, and hence utility, of the method.

The experiments are in general well-described. The manuscript contains clear figures, and also details about dimensions and flow rates used, which always help in doing quick calculations of residence times, etc. The manuscript itself contains some errors and inconsistencies, which will be detailed below. Of course, the simultaneous measurement of rate coefficients by the relative rate method is not new. Kramp and Paulson [J. Phys. Chem. A, 102, 1998, 2685-2690] reacted mixtures of hydrocarbons in Teflon bags to evaluate systematic uncertainties between reference compounds. However, to the best of my knowledge, this has not been done in a flow reactor until now.

Kramp and Paulson (1998) used mixtures of three compounds to measure two reference reactions relative to a single target reaction. The target *k* value was calculated using the reference to target ratios individually, as done in the traditional relative rate method. The method presented in this work differs in that it uses multiple reference reactions to generate a multi-variate relationship, which is then used to derive new *k* values relative to all other reactions.

The biggest issue with the manuscript is that the method is not actually universal, since the derived rate coefficient is dependent on the reactivity of the mixture and the extent of conversion. Thus, it appears that knowledge of the rate coefficients is almost required in order to put them on an absolute basis.

Rate coefficients do not depend on reactivity, rather reactivity depends on rate coefficients (see Eq. (4) in the manuscript). Nor do rate coefficients depend on the extent of the conversion of the reactants. However, the rate of a reaction does depend on the extent of conversion; as the reactants are reduced in concentration, the number of collisions reduces. Therefore, the reactor does not suffer the issues suggested by the referee, and has a wide utility for VOCs of differing reaction rates with OH.

For this reason, I find that the methodology would have limited applicability to other systems. For example (and this is touched on in the manuscript) in ambient air samples the reactivity can vary widely, and so one needs to know whether the response will be linear or not. Also, if someone else were going to set up a similar experiment, would they have to characterize their system with curves such as those shown in Figure 4? The manuscript does not really answer these questions and reads a little like a work in progress for me, at least.

The reactivity of ambient air samples can vary greatly. However, knowing the response (in terms of depletion factor to rate coefficient) is not necessary prior to experiment. Therefore, new reactors could be developed by other groups and applied to novel systems. The key here is that plotting a consistent function through the data allows for the extraction of relative rate data, regardless of whether it is a linear or curved function. A linear function is desirable, as this makes data analysis much easier, but not necessary.

For these reasons I can not recommend publication of the manuscript in its current form. Minor corrections follow (format Page/Line).

We feel that the explanations provided above counter the referee's concerns. The reactor has wide applicability and can be used without prior knowledge of the shape of the depletion factor versus *k* response.

Page 4/14. The subject of this sentence is "this parameter" (i.e. the reactivity) so it should not vary from milliseconds to tens of seconds.

The manuscript has been amended to read "*This parameter is equivalent to the inverse of the lifetime of the OH radical which can vary greatly depending on total VOC loading, from milliseconds in heavily polluted areas, to tens of seconds in clean air*" to clarify that the subject should be the OH lifetime.

Page 4/18. I would imagine that lack of knowledge of the identity of VOCs is more responsible for missing reactivity than errors in the rate coefficients?

The authors agree that the errors in *k* values are not the issue with the 'missing reactivity', although the sentence in question does not specifically mention errors themselves being the problem. OH reactivity is calculated by combining the concentration of a particular VOC with its rate coefficient for reaction with OH. Hence, the composition of the atmosphere must be known but the identity of each VOC is not strictly needed, although it does help for targeting the measurement of the OH + VOC *k* value.

The manuscript has been clarified to read: "*It is thought that a lack of detailed compositional information and corresponding kinetic data for many OH + VOC reactions may contribute to the so-called "missing reactivity" that has been observed both locally and globally (Lidster et al., 2014).*"

Experimental section. Sometimes cc are used, sometimes ml for volume. Please be consistent.

This has been amended for consistency and the manuscript now contains exclusively 'cm^3'.

Page 8/3. Remove "a" before "magnitude".

Amended.

Page 8/25, and caption for Figure 2. It says here and in the caption that black is lamp off, blue is lamp on, while in the following sentence and the Figure legend this is reversed (and presumably correct).

Amended.

Page 9/12, and caption for Figure 3. OH reactivity is given as 180 in text, 240 in Figure caption.

Amended. It should have been 240 s^{-1} and the text has been clarified to reflect this.

Page 12, paragraph starting on line 19. This is a little confusing. By non-Arrhenius, I presume you mean having a negative activation energy. This would be expected for addition reactions. However, the last sentence does not really make sense. I do not know if the differences you see are meaningful at this level of precision.

The sentence has been amended to "*This reflects the temperature dependent relationship described and observed in the literature for OH addition to alkenes and monoterpenes (Chuong et al., 2002; Kim et al., 2011).*"

It is difficult to extract meaningful differences between the measured values for *k* at 298 K and at 323 K. See below for more discussion.

Page 12/27. I would think that all OH + alkane rate coefficients would show a "normal" activation energy, linear, cyclic or branched.

The sentences attempting to derive meaningful kinetic information from the *k* values measured at 298 K and 323 K have been removed. The authors agree that it is difficult to extract meaningful differences between the measured values for *k* at 298 K and at 323 K, with the current level of precision.

The section now focuses on the fact that for some of these compounds no 298 K data currently exists and hence, this 323 K data represents our best estimate for room temperature reaction rates.

The section now reads: "*Rate coefficients for the reaction between OH and 12 aromatic VOC at 323 K are also estimated for the first time. We are also able to derive 323 K rate coefficients for the reaction between OH and three alkanes (2-methylheptane, 3-methylheptane and ethylcyclohexane) for which we could find no 298 K data in the literature. This highlights the pressing need for relevant temperature dependent rate coefficient data.*"

Fig 6 Noshino should be Nishino

Amended.

McGillen (2008) is missing from ref list

Amended.

A self-consistent, multi-variate method for the determination of gas phase rate coefficients, applied to reactions of atmospheric VOCs and the hydroxyl radical

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Abstract. Gas-phase rate coefficients are fundamental to understanding atmospheric chemistry, yet experimental data are not available for the oxidation reactions of many of the thousands of volatile organic compounds (VOCs) observed in the troposphere. Here a new experimental method is reported for the simultaneous study of reactions between multiple different VOCs and OH, the most important daytime atmospheric radical oxidant. This technique is based upon established relative rate concepts but has the advantage of a much higher throughput of target VOCs. By evaluating multiple VOCs in each experiment, and through measurement of the depletion in each VOC after reaction with OH, the OH + VOC reaction rate coefficients can be derived. Results from experiments conducted under controlled laboratory conditions were in good agreement with the available literature for the reaction of nineteen VOCs, prepared in synthetic gas mixtures, with OH. This approach was used to determine a rate coefficient for the reaction of OH with 2,3-dimethylpent-1-ene for the first time; *k* = 5.7 (± 0.3) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. In addition, a further seven VOCs had only two, or fewer, individual OH rate coefficient measurements available in the literature. The results from this work were in good agreement with those measurements. A similar dataset, at an elevated temperature of 323 (± 10) K, was used to determine new OH rate coefficients for twelve aromatic, five alkane, five alkene and three monoterpene VOC + OH reactions. In OH relative reactivity experiments that used ambient air at the University of York, a large number of different VOCs were observed, of which ~~23~~twenty-three were positively identified. ~~19~~Nineteen OH rate coefficients were derived from these ambient air samples, including ten reactions for which data was previously unavailable at the elevated reaction temperature of *T* = 323 (± 10) K.

1 Introduction

The atmosphere is an extremely complex and reactive mixture containing large numbers of inorganic and organic chemicals (Lewis et al., 2000; Goldstein and Galbally, 2007). Annually, over 1000 Tg of VOCs are emitted to the troposphere from both anthropogenic and biogenic sources (Guenther et al., 2002). They have wide-ranging impacts on human health, either directly on inhalation, or through their photochemical degradation cycles, which generate polluting and radiatively active secondary products such as ozone and aerosols. Atmospheric oxidative removal of most VOCs is mainly initiated by gas-phase reaction with the hydroxyl radical (OH). This process determines the tropospheric lifetime of an organic compound and often represents the rate-determining step in tropospheric ozone production and photochemical smog formation (Finalyson-Pitts and Pitts Jr., 1997). Photochemical models used for air quality forecasting and future climate predictions can only attempt to represent these processes if provided with accurate rate coefficients for OH + VOC reactions. Thus, this aspect of gas-phase kinetics represents a fundamental pillar of atmospheric and, more widely, environmental science (Burkholder et al., 2017).

Many hundreds of reactions for the OH initiated degradation of VOCs have been measured in the laboratory. However, many thousands more VOCs are emitted, or are formed in atmospheric photochemical oxidation, for which no OH kinetics have been measured. ~~In order to~~To bridge the gap between our limited ~~fundamental~~ experimental knowledge, and the detailed chemical mechanisms required to describe the ~~chemical schemes~~chemistry employed in air quality ~~and climate~~ models, a number of methods have been developed to estimate rate coefficients for ~~unmeasured species, including~~the reactions of OH ~~oxidation~~with VOCs (Atkinson, 1986; Kwok and Atkinson, 1995; Ziemann and Atkinson, 2012). A structure-activity relationship (SAR) relates parameters such as the rate coefficient to the structural properties of chemical species, thereby providing a semi-empirical method of parameter estimation which does not rely on experimentation. SARs are developed from datasets of experimentally derived parameters, and therefore require accurate and reliable kinetic information from a wide range of organic reactions (in terms of both structure and functionality) to derive the various group rate coefficients and substituent factors needed (Calvert et al., 2002).

Almost all experimental OH + VOC kinetic data used for atmospheric science have been determined via measurements conducted in controlled laboratory environments. Absolute methods for determining rate coefficients, such as flash photolysis and discharge flow, rely on accurate observations of the VOC concentration, which is maintained in large excess over that of OH (Pilling and Seakins, 1995). Much of the difficulty associated with these methods is related to the direct monitoring of the short-lived OH radical. Alternatively, the relative-rate method requires neither an accurate knowledge of VOC concentration, nor direct monitoring of OH radicals (Atkinson, 1986). This technique instead relies on the simultaneous measurement of two species: a target VOC that is the focus of the investigation, and a well characterised reference compound, which ideally ~~react at a~~possess similar rate coefficients for reaction with OH. Upon exposure to OH, these two VOCs are depleted relative to their individual rate coefficients. Thus, the ratio of their depletion allows for the calculation of the target rate coefficient, providing the OH + reference VOC rate coefficient is accurately known and the losses of both compounds in the reactive system are solely governed by reactions with OH. Traditionally, both absolute and relative-rate methods have been used to obtain rate coefficients for one OH + VOC reaction at a time; as a result, these methods are time consuming and few laboratories are capable of sustaining this type of fundamental science.

Whilst measured rate coefficients for reactions of OH with simple short-chain VOCs (up to seven carbon atoms) have been measured and evaluated at least once, and some many times over, data for many larger, more complex and multifunctional VOCs are often poorly constrained or unmeasured. Recent observations in a megacity demonstrate that VOCs containing more than seven carbon atoms can make up greater than 50% of the local atmospheric hydrocarbon mass and dominate secondary organic aerosol (SOA) production (Dunmore et al., 2015). As the number of carbon atoms increases, so does the relative complexity of the oxidation reaction scheme, and hence the photochemical potential to form secondary pollutants such as ozone and SOA. As we discover more concerning the complexity of atmospheric ~~VOCs~~VOC chemistry, the database for OH + VOC rate coefficients appears increasingly deficient. Conventional laboratory methods, limited to studying a single VOC at a time, are no longer adequate and as such new approaches and techniques are required.

Comprehensive measurements of each individual VOC + OH reaction rate coefficient can be avoided by using direct OH reactivity measurement techniques to measure the total OH reactivity sink. This parameter is equivalent to the inverse of the lifetime of the OH radical ~~and~~which can vary greatly depending on total VOC loading, from milliseconds in heavily polluted areas, to tens of seconds in clean air (Yang et al., 2016). Techniques using direct laser induced fluorescence (LIF) detection of OH first identified a significant mismatch between measured and modelled OH reactivities (Kovacs et al., 2003; Di Carlo et al., 2004, Edwards et al., 2013). More recently, a technique that does not require the direct observation of OH radicals, termed the comparative reactivity method (CRM), has been developed (Sinha et al., 2008). It is thought that a lack of detailed compositional information and corresponding kinetic data for many OH + VOC reactions may contribute to the so-called 'missing reactivity' that has been observed both locally and globally (Lidster et al., 2014).

We describe here an experimental technique capable of measuring rate coefficients for large numbers of OH + VOC reactions simultaneously, which builds upon a method employed by Kato et al. (2011) to measure the contribution of unidentified VOCs to OH reactivity. Coupling a conceptually simple and internally self-consistent relative rate kinetic method to modern automated analytical equipment allows for the study of a wide range of species, including some that are difficult to measure using more conventional methods. ~~Rather than rely on one reference VOC, a~~A subset of the existing OH + VOC kinetic database is used to place the experimental relative rate data on an absolute scale, thereby reducing ~~uncertainties.~~the reliance on a single reference reaction. A broad range of OH + VOC reactions were studied, comparisons with the literature made and rate coefficients for previously unmeasured OH + VOC reaction determined at two reaction temperatures.

2 Methodology

Experiments were conducted under ~~near ambient~~ conditions ~~(*P* =~~of 1~~.0~~ bar (N_2~~), *T* = 295~~) and 298-323 K~~)~~ in a stainless steel flow reactor (approximate external dimensions 470 × 25 × 25 mm, internal volume 250 cm^3). A schematic of the apparatus is shown in Fig. 1. A quartz window, positioned on the top face of the reactor, allowed collimated vacuum-ultraviolet (VUV) light from a low-pressure Hg/Ar lamp (L.O.T., Pen-Ray®) to enter the tube. N_2 (2000 standard ~~cubic centimetres~~cm^3 min^{-1} (sccm)) was passed through a bubbler filled with high purity water (Fischer, Optima grade) and supplied to the reactor upstream of the quartz window via a mass flow controller (MKS). OH was generated in the reaction chamber via the photolysis of H_2O via R1. Atomic H is rapidly converted to HO_2 via R2. The oxygen is found as impurities in the N_2 carrier gas.

$$\mathrm{H_2O} + h\nu\ (184.95\ \mathrm{nm}) \rightarrow \mathrm{OH} + \mathrm{H} \qquad \text{(R1)}$$

$$\mathrm{H} + \mathrm{O_2} \cancel{\rightarrow} + \mathrm{M} \rightarrow \mathrm{HO_2} \text{———} + \mathrm{M} \qquad \text{(R2)}$$

The VOC mixture was introduced downstream of the quartz window via a stainless-steel injector (external diameter 3.2 mm) to avoid unwanted removal of organics via photolysis. A sliding injector allowed for the optimisation of the inlet location with respect to both minimising the effects of VUV photolysis and maximising exposure to the short-lived OH radicals (Cryer, 2016). Mixing of the VOC flow (200-1000 sccm) with the main OH / H_2O / N_2 flow was aided by the injector design, which ensured that VOCs pass into the main body of the reactor via an array of four holes radially distributed about the injection tube. The flow of the VOC mixture~~, along with~~ and a secondary flow of N_2, were controlled by two mass flow controllers (Tylan), allowing for the variation of VOC mixing ratio in the reactor. This meant that testing samples with a range in total VOC loading and OH reactivity was possible. A brief outline of the estimated range in total VOC concentrations and OH reactivity of each mixture injected into the reactor can be found in Supplementary Information Table S1. Assuming a constant total flow rate of 3000 sccm the residence time of the VOCs in the reactor was calculated to be approximately 4 s, of which OH is estimated to persist for no longer than 0.5 s.

By alternating between the lamp switched off and the lamp switched on, a set of observations ~~was~~were generated that could be split into two unique datasets; those with OH initiated depletion and those without. ~~The~~Assuming consistent trapping and sampling with both the lamp switched off and the lamp switched on, the depletion of an individual VOC, with a known OH rate coefficient can be evaluated using simple kinetic equations. This is shown using isoprene as an example in Eqs. (1), (2) and (3). The depletion factor in a VOC due to reaction with OH ($\ln\left(\frac{[\mathrm{VOC}]_0}{[\mathrm{VOC}]}\right)$) can be related to its rate coefficient, *k*, as shown in the example in Eq. (3).

$$\text{isoprene} + \mathrm{OH} \overset{k_2}{\rightarrow} (\text{products}) \qquad \text{(R3)}$$

$$\frac{\mathrm{d[isoprene]}}{\mathrm{dt}} = -k_2[\mathrm{isoprene}][\mathrm{OH}] \tag{1}$$

$$\frac{\mathrm{d[isoprene]}}{\mathrm{[isoprene]}} = -k_2[\mathrm{OH}]d\mathrm{t} \tag{2}$$

$$\ln\left(\frac{[\mathrm{isoprene}]_0}{[\mathrm{isoprene}]_\mathrm{t}}\right) = k_2\int[\mathrm{OH}]_\mathrm{t}d\mathrm{t} \tag{3}$$

The integral of OH concentration over time ($\int[\mathrm{OH}]_\mathrm{t}d\mathrm{t}$) is known as the OH exposure (OH_{exp}). The assumption is that all VOCs in the sample experience identical exposure to OH radicals owing to rapid homogenous mixing in the reactor. However, ~~despite~~because of the establishment of laminar flow in the reactor~~,~~ (Re = 132), thorough and complete mixing of OH is unlikely to take place~~.~~ (see Supplementary Information). When using reactive gas mixtures containing VOCs which react rapidly with OH, a non-linear relationship between ~~$\ln\left(\frac{[\mathrm{VOC}]_0}{[\mathrm{VOC}]}\right)$ and *k* may be observed, as compounds experience differing exposures to OH. Slow reacting VOCs may experience a larger exposure to OH relative to faster reacting VOCs.~~depletion factor and *k* may therefore be observed (see Supplementary Information). However, this does not represent a limitation to the technique. So long as a relationship between $\ln\left(\frac{[\mathrm{VOC}]_0}{[\mathrm{VOC}]}\right)$ and *k* can be characterised over a range of rate coefficients, and the data placed on an absolute scale, relative rate results can still be extracted.

Assuming that a relationship between $\ln\left(\frac{[\mathrm{VOC}]_0}{[\mathrm{VOC}]}\right)$ and *k* can be identified, a previously unknown OH rate coefficient, k_X, for a specific target VOC, X, can be calculated using multiple known *k* values as references. An unknown OH rate coefficient will be subject to less uncertainty if its value is interpolated rather than extrapolated and compounds at the extreme upper and lower limits of the observed relationship will be subject to greater uncertainty. Regardless, the use of multiple known *k* values should ~~minimise~~reduce the reliance on any ~~systematic error induced compared with using a~~ single reference ~~compound~~reaction.

2.1 Choice of reference *k* values

Some VOCs have literature measurements from two or more laboratories and these can differ considerably. The choice of different reference values for placing the relative rate measurements on an absolute scale can lead to variations in the final outcome of the experiment. When deciding on reference literature values for use in these experiments, a number of sources were utilised. The IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (http://iupac.pole-ether.fr/) provides recommended values for the reaction between OH and many short chain hydrocarbons, along with some common monoterpene and aromatic VOCs (Atkinson et al., 2006). These values are evaluated using a balance of literature data and are updated regularly and so this data was prioritised. Atkinson and Arey (2003) provide a reviewed dataset for a larger number of VOCs, collated from several sources, including the extensive evaluations on atmospheric oxidation of alkenes and atmospheric oxidation of aromatic hydrocarbons in Calvert et al. (2000) and Calvert et al. (2002) respectively. In the case that a reference value was not found in the IUPAC Kinetic Data Evaluation, Atkinson and Arey (2003) was used. Reference values at 298 K for only two compounds (1-nonene and 1-octene) could not be found in either the IUPAC evaluated database or Atkinson and Arey (2003). Reference values for these compounds were therefore sourced from Aschmann and Atkinson (2008).

In some cases, the recommendations found in Calvert et al. (2000, 2002) were based upon a single relative rate experiment. The results of those experiments were often based upon outdated recommended rate coefficients for the reference compounds used. As such, and to ensure consistency, the reference values used in this work were updated to reflect any changes in the original relative rate compounds used in those experiments (see Tables 1, 2 and 3 for details).

Evaluated literature reference values for all the compounds used can be found in Tables 1, 2 and 3. VOC depletion factor ($\ln\left(\frac{[\mathrm{VOC}]_0}{[\mathrm{VOC}]}\right)$) was plotted against these literature values using Eq. (3) and weighted linear regression, using QR decomposition, performed to find the OH exposure (OH_{exp}).

2.2 Gas sampling and analysis

VOCs emerging from the reactor were collected using a Unity 2 thermal desorption unit (TDU) fitted with a Tenax TA sorbent trap and a CIA 8 Air Server attachment (Markes International). The system was pre-purged at a flow rate of 100 cm^3 min^{-1} for six to ten minutes before sampling. During sampling, the trap was maintained below -20 °C and a sampling flow rate of 100 cm^3 min^{-1} used for one minute to give a total sample volume of 100 cm^3. After sampling, the system lines and sorbent trap were purged with helium carrier gas for three minutes at 100 cm^3 min^{-1} to eliminate oxygen from the system before desorption onto the GC column. During the desorption process, the trap was rapidly heated to 250 °C and held for three minutes. All flow paths and sample lines were heated to 150 °C.

The GC system was an Agilent 6890 (Agilent Technologies) 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. Column head pressure was set to 344 kPa (50 psi) and operated in constant pressure mode using helium as a carrier gas. The temperature ramping of the GC oven was varied between mixtures to achieve optimum separation of VOCs. The GC method and TDU setup gave sample turn arounds of up to 70 minutes for more complex mixtures, and up to 20 minutes for simpler mixtures.

2.3 Synthetic Mixtures

Three synthetic gas mixtures were tested using the method outlined above, in which the compounds included in the mixtures, their preparation and the conditions under which they were tested differed. Differences in the reactivity of the VOCs within each mixture were distinguished by calculating the total OH reactivity for that mixture. The OH reactivity for each mixture was calculated as the total sum of each of the reference k values multiplied by the VOC's concentration as shown in Eq. (4). This parameter is not necessary for the measurement of k values but is provided in order to differentiate between individual mixtures and also between the same mixture studied under different flow regimes.

$$\text{OH reactivity} = \sum k_{\mathrm{VOC}_i+\mathrm{OH}}[\mathrm{VOC}_i] \tag{4}$$

Mixture 1 was prepared by injecting 1-5 ~~µl~~mm^3 of undiluted liquid VOC into a 500 ~~ml~~cm^3 evacuated, double ended, stainless-steel sample cylinder (Swagelok). This cylinder was flushed into a pacified gas cylinder (10 L, Experis, Air Products) and filled to approximately 20 bar with N_2. The cylinder was then evacuated to atmospheric pressure before being refilled to approximately 100 bar with N_2 to achieve a final mixing ratio of each VOC in the cylinder of an estimated 30 parts per billion by volume (ppbv). **Mixture 1** consisted of mainly monoterpenes, along with *m* and *o*-xylene (Table 1), and was studied at room temperature (average reaction T = 294.5 (± 1.5) K). There was only a small range in OH + VOC rate coefficients and this mixture did not contain any compounds without a literature rate coefficient. The estimated total OH reactivity at standard temperature and pressure (STP) of the VOCs contained in **Mixture 1** was 900 s^{-1}. This mixture was diluted with N_2 in differing amounts in order to inject gaseous samples into the reactor with a range of OH reactivities between 50 and 300 s^{-1}.

Mixture 2 was prepared using the same method as that used for **Mixture 1** and was also introduced into the reactor at room temperature (294.5 (± 1.5) K). The VOCs in this mixture comprised primarily 1-alkenes and cycloalkenes (Table 2) with a range of OH rate coefficients spanning less than a single order of ~~a~~ magnitude. One compound, 2,3-dimethylpent-1-ene, had no reported rate coefficient with OH at room temperature~~.~~ at the time of writing. The estimated total OH reactivity at STP of VOCs contained in **Mixture 2** was 480 s^{-1}. This mixture was diluted with N_2 in differing amounts to inject gaseous samples into the reactor with a range of OH reactivities between 25 and 150 s^{-1}.

Mixture 3 was prepared by adding between 1-5 µg, or 1 ~~µl~~mm^3, of each individual solid or liquid VOC to a 25 ~~ml~~cm^3 headspace vial. 200 ~~µl~~mm^3 of the mixture vapour was then added to a 500 ~~ml~~cm^3 evacuated, double ended, stainless steel sample cylinder (Swagelok). This cylinder was flushed into a pacified gas cylinder (Experis, Air Products) and filled to approximately 200 bar with ambient air using an oil free, modified RIX compressor (RIX Industries). This mixture contained 43 species, grouped as biogenics, alkenes, alkanes and aromatics (Table 3). The vapour pressure of each compound was used to approximate its concentration in ppbv in the final mixture, to allow for an estimation of the total OH reactivity of the whole mixture of 380 s^{-1} (at STP). To facilitate consistent transmission of low vapour-pressure VOCs through the reactor, **Mixture 3** was introduced at an elevated temperature of 323 (± 10) K. This temperature was achieved by wrapping the reactor in heat tape, and measured using a Type K mineral insulated thermocouple (TCDirect, p/n 408-059) inserted into the reactor.

3 Results and Discussion

Synthetic gas mixture results are presented in Sect. 3.1 and 3.2. Results taken from the more complex sampling of ambient air are presented in Sect. 3.3, along with an outline of the adjusted experimental setup. The errors, equal to 1σ (66%), quoted on the measured values in this work are the statistical uncertainties calculated by combining the instrument error and the scatter in the $\ln\left(\frac{[\mathrm{VOC}]_0}{[\mathrm{VOC}]}\right)$ vs. k data. However, the uncertainties reported in the evaluated literature rate coefficients used as relative rate reference compounds are often large; up to 35% in some cases (Calvert et al., 2002). Using these values for the reference compounds therefore places a limitation on the precision of the results in this work that is not captured by the quoted uncertainties.

3.1 Results from relative rate experiments at 295 K

Figure 2 shows sections of typical total ion chromatograms (TIC) obtained for **Mixture 1**; one chromatogram with the reactor lamp turned off (~~black~~blue) and one for a sample with the reactor lamp turned on (~~blue~~black). When exposed to OH radicals (black), there is a clear reduction in the observed concentration of all VOCs present, reflected in the reduction in peak areas compared with lamp off (blue). The use of selected ion chromatograms provides a clear advantage of using a TOF-MS over a less specific detector due to the reduction in background interference and ease of peak identification. Peak areas were analysed automatically using peak integration software (Agilent Technologies) with appropriate mass ion selection for each VOC. This allowed for the complete separation of peaks which may otherwise have been unresolved.

To ensure that the observed depletion in each VOCs concentration was entirely due to reaction with OH, experiments were performed in the absence of the OH precursor (i.e. the water bubbler was removed from the system). When the lamp was switched on there was no significant deviation observed in the peak areas for any of the VOC used. As a result, both direct photolysis of VOC and unwanted perturbations due to the lamp (such as heating effects) were deemed to be negligible. However, other possible perturbations, such as those due to reaction of the VOCs with other photooxidants, could not be ruled out using this method.

Experiments were conducted on each VOC mixture using different mass flow controller settings, allowing for the injection of mixtures into the reactor with five different total VOC loadings, and hence five different total OH reactivities. GC-MS data were analysed using automatic peak integration software and outlying peak areas recommended and removed using the $\mathrm{MAD_e}$ method (Burke, 2001).

Figure 3 shows the relationship between experimentally observed $\ln\left(\frac{[\mathrm{VOC}]_0}{[\mathrm{VOC}]}\right)$ and literature rate coefficients for **Mixture 1** with an OH reactivity of ~~180~~240 $\mathrm{s^{-1}}$. A clear correlation between k and $\ln\left(\frac{[\mathrm{VOC}]_0}{[\mathrm{VOC}]}\right)$ can be seen ($R^2 = 0.96$). The nature of Eq. (3) suggests that the fit should be proportional, with an intercept of zero. However, despite the intercept ~~being~~lying close to zero, linear fits with a non-zero intercept were found to be a more appropriate approximation~~.~~ across the range of *k* values measured. Extrapolation beyond the range of reference OH + VOC *k* values is not necessary to make accurate measurements of *k* values. For the calculation to be valid, there needs ~~to~~ only to be a consistent relationship between the depletion ~~of~~factor for each VOC and k. For **Mixture 1** with a low OH reactivity (50 $\mathrm{s^{-1}}$), a three-parameter exponential distribution function, given in Eq. (5) was used to fit the data, shown in Fig. 4. Whilst this is inconsistent with Eq. (3), it does not necessarily detract from the relative rate nature of the experiment as a reliable and consistent function can still be plotted through the data. This type of distribution possibly occurs when gas mixtures contain low concentrations of very fast reacting VOCs and arises due to poor mixing conditions within the reactor~~.~~ (see Supplementary Information). As this was only observed during some experiments, the relative rate data obtained from these plots were disregarded.

$$y = e^{a+\frac{b}{x+c}} \qquad (5)$$

The gradient of the line in Fig. 3 is~~ equal to~~ the OH_{exp}, the integral of OH concentration over time~~.~~ (see Eq. 3). OH_{exp} ~~generally~~ decreased with the increasing OH reactivity of the gas mixture injected (see Supplementary Information Fig. ~~S1). This is in line with other studies by Li et al. (2015) and Peng et al. (2015), who found that increasing the OH reactivity results in an increased rate of removal of OH radicals from the system. The integral of the OH concentration over time is reduced upon increasing the OH reactivity due to the increased number of OH + VOC reactions taking place.~~S6).

~~Using Eq. (3)~~

By referring to a generalised version of Eq. (3), and using the function of the weighted linear regression, it is possible to estimate new *k* values at room temperature (295 (± 2) K) for all components in **Mixture 1** relative to each other. As OH_{exp} is dependent on the OH reactivity of the mixture introduced into the reactor, it is necessary to produce a *k* value for each VOC at each mass flow controller setting. An error weighted mean of the individual *k* values determined at each OH_{exp} was then used to assign a final measured OH rate coefficient for each VOC in the mixture (Table 1).

The majority of VOCs show ~~rates~~rate coefficients consistent with those in our evaluated literature data set, within experimental error and literature uncertainty. Thus, this technique represents an extension of the classical relative-rate experiment but with the advantage of using multiple species to generate a multivariate, self-consistent relationship between the ~~loss of~~depletion in a VOC and its rate coefficient for reaction with OH, rather than using just one pair of compounds at a time (reactant + reference). By using multiple reference compounds, the risk of a single erroneous reference value perturbing the rest of the data is reduced, assuming that all compounds behave in ~~the same~~a similar way upon exposure to OH. This advantage does come at the expense of a loss in traceability; when changes are made to the reference rate coefficient for a specific measurement it is relatively easy to propagate the uncertainty change through to the relative rate measurements. When using multiple reference reactions, and generating a relationship between them, the transfer of an updated rate coefficient change would obviously be more complicated.

Whilst the majority of our data is in good agreement with the internally consistent literature data set, the wider literature contains rate coefficient measurements for many of the compounds not included in the IUPAC evaluations or the review paper, Atkinson and Arey (2003). For example, a recent measurement of the oxidation of β-ocimene by OH provided a rate coefficient of 236 (± 54) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, which is in good agreement with our own result for the same reaction, of ~~222 (± 7~~223 (± 10) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Gaona-Colmán et al., 2016). Recent relative rate measurements of the OH + myrcene reaction~~ rate,~~ by Hites and Turner (2009) and Kim et al. (2011) are 50% greater than that calculated in this work. However, their measurements of 335 ($^{+\,144}_{-\,101}$) and 334 ($^{+\,220}_{-\,132}$) × 10^{-12} cm^3 molecule^{-1} s^{-1} respectively, have exceptionally large uncertainties that ~~encompasses~~encompass the measurement presented in this paper, of ~~204 (± 7~~206 (± 8) × 10^{-12} cm^3 molecule^{-1} s^{-1}. Our measurement of the rate coefficient for the reaction of limonene ~~oxidation rate~~with OH is also in good agreement with the recent value in Braure et al. (2014), of 165 (± 25) × 10^{-12} cm^3 molecule^{-1} s^{-1}.

The measured ~~value~~rate coefficient for the OH + *o*-xylene reaction, of ~~1.6 (± 1.0~~4.8 (± 7) × 10^{-12} cm^3 molecule^{-1} s^{-1} is the only result which is not totally consistent with the literature. It is likely that this ~~is an erroneous measurement that~~anomaly arose due to ~~the OH initiated depletion of~~ *o*-xylene being ~~too small and subject to large relative errors~~at the lower extreme of the mixture reactivity. It was therefore removed from subsequent analyses.

Figure 5 shows an example relative rate plot for **Mixture 2**; for which a linear relationship is observed across all OH reactivities tested. *k* values for all the VOCs in this mixture can be estimated using ~~Eq.~~the generalised form of Eq. (3). These values are given in Table 2 and are all consistent with our evaluated literature data set whereas other literature measurements for the OH + cyclohexene and the OH + cyclopentene reactions, of 54 × 10^{-12} and 45 × 10^{-12} cm^3 molecule^{-1} s^{-1} respectively, are much smaller than our own estimations (Rogers, 1989). Figure 6 demonstrates that our measured rate coefficients for the reactions of OH with 1-alkenes agree well with both experimentally-derived literature rate coefficients and those estimated from structure activity relationships. Whilst we do not observe a strictly linear trend between *k* values - and increasing carbon chain length for the 1-alkenes, most of our measurements lie between the SAR predictions of Kwok and Atkinson (1995), Peeters et al. (1999, 2007) and Nishino et al. (2009) and are in good agreement with other experimental measurements.

Mixture 3 contained a much broader range in VOCs, both in terms of functionality and structure, but also in terms of *k* values. Unlike **Mixtures 1** and **2**, the values for *k* spanned almost two orders of magnitude; from slow reacting alkanes such as *n*-heptane, literature *k* = 7.2 ($^{+\,2.0}_{-\,1\cancel{.6}.6}$) × 10^{-12} cm^3 molecule^{-1} s^{-1}, to faster reacting monoterpenes such as limonene, literature *k* = 170 (± 51) × 10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003). The concentrations of the individual VOCs in the mixture were also much lower compared with the other mixtures. Both the complexity of the mixture and the low concentration of the constituents make this mixture more representative of ambient atmospheric conditions. This mixture was studied at an elevated reactor temperature of *T* = 323 (± 10) K in order to ~~prevent excessive~~avoid greater uncertainties as a result of partitioning of the less-volatile VOCs to the reactor ~~walls~~surfaces.

Figure 7 shows the results of a relative rate experiment for **Mixture 3**. Only compounds with a known rate coefficient at 323 K are shown. The relationship between VOC depletion factor ($\ln\left(\frac{[\mathrm{VOC}]_0}{[\mathrm{VOC}]}\right)$) and *k* shows an exponential cumulative distribution, likely due to the small concentrations of VOCs injected and the large range in VOC + OH rate coefficients. The inset shows that it is possible to approximate the rate ~~of VOC + OH~~coefficient for ~~species~~reactions with a *k* value (at 323 (± 10) K) of less than 30 × 10^{-12} cm^3 molecule^{-1} s^{-1} (corresponding to a depletion factor of less than 0.4) using linear regression. ~~Using this method, the~~The rate coefficients estimated using both the curved relationship and linear regression are in very good agreement, within errors. The estimated *k* values for many of the VOCs in **Mixture 3** are also consistent with those in the literature (Table 3), suggesting that measurements at close to ambient atmospheric conditions are possible. ~~Two measurements stand~~One measurement stands out as contrasting with ~~their~~its literature ~~values~~value; that for ~~myrcene, of 310 (± 105) × 10^{-12} cm^{3} molecule^{-1} s^{-1} and that for~~ β-ocimene, of 950 (± 800) × 10^{-12} cm^{3} molecule^{-1} s^{-1}. ~~These two compounds were~~This compound was at the higher end of the reactivity scale in **Mixture 3**, and hence small deviations in ~~their~~its depletion would lead to large variations in ~~their~~its measured ~~values~~value using the derived curved relationships. This is reflected in the comparatively large errors relative to the other VOCs in the mixture. Similar to *o*-xylene in **Mixture 1**, the results for ~~these two compounds~~this compound were removed from subsequent analyses.

Figure 8 shows an overall plot of all measured rate coefficients taken from **Mixtures 1, 2** and **3** plotted against their literature reference counterparts. Solid data points are for measurements made at 294 (± 2) K whilst empty data points are for measurements conducted at the elevated reactor temperature of 323 (± 10) K. The black solid line represents a 1:1 fit. Linear regression may be performed on the dataset in its entirety to determine the overall ability of this method for replicating literature rate coefficients. The gradient of this regression is 1.0 (± 0.02) which suggests that this experimental technique is able to replicate the literature exceptionally well. The vast majority of data lie well within an uncertainty in the literature of 25%, shown by the grey shaded area. Outliers include: 1-hexene at room temperature and 2,2,3-trimethylbutane~~,~~ and *n*-nonane~~ and β-pinene~~ at 323 K.

Our studies suggest that a linear response between ln $\left(\frac{[\mathrm{VOC}]_0}{[\mathrm{VOC}]}\right)$ and *k* is best achieved when the VOCs in a mixture have a small range in OH rate coefficients (i.e. they react with OH at similar rates, with respect to each other). It appears that a non-linear response occurs when the mixing of VOCs and radicals are on similar timescales to the chemistry. Therefore, mixtures that satisfy the above criteria are preferred for the estimation of novel rate coefficients, as demonstrated using **Mixture 2**. Whilst there is still a~~ good~~ correlation between ln $\left(\frac{[\mathrm{VOC}]_0}{[\mathrm{VOC}]}\right)$ and *k* for mixtures which do not satisfy this criterion, the non-linearity makes the estimation of novel rate coefficients more challenging, but still possible. These mixtures may therefore be better suited for highlighting inconsistencies within the current literature data set for certain groups of compounds.

3.2 Determination of new rate coefficients

Mixture 2 contained the compound 2,3-dimethylpent-1-ene, for which we could find no literature rate coefficient measurements at the time of writing. 2,3-dimethylpent-1-ene has been detected in emissions from certain tomato variants cultivated in Portugal (Figueira et al., 2014). Using a generalised version of Eq. (3), it is possible to estimate an experimentally derived room temperature OH rate coefficient for this compound of k = 57 (± 3) × 10^{-12} cm^{3} molecule^{-1} s^{-1}. As discussed earlier in Sect. 3, the error in this value is the statistical uncertainty calculated by combining the instrument error and the scatter in the data. However, the calculation of measurement uncertainty does not reflect the larger

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uncertainties, of up to 35%, in the rate coefficients used as reference compounds and can therefore be considered an underestimation (lower limit) of the true uncertainty.

SARs are often used to predict rate coefficients for those compounds which do not have experimentally determined values. Three distinct SARs in the literature can be used to estimate a rate coefficient for 2,3-dimethylpent-1-ene. Using the methods outlined in Kwok and Atkinson (1995), Peeters et al. (1999, 2007) and Nishino et al. (2009), the rate coefficient for 2,3-dimethylpent-1-ene can be estimated as k = 55.0, 63.1 and 59.3 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} respectively. These are all in good agreement with the experimental measurement made in this work.

Using the same method for **Mixture 3,** k values at 323 K for 20 compounds, as yet unmeasured at this temperature, can be calculated (Table 3). However, the straight line becomes increasingly less appropriate for estimating new rate coefficients at higher VOC depletion factor as the linear regression begins to deviate further from the data. Table 3 therefore also provides rate coefficients for all the compounds in **Mixture 3** calculated using the equation of a curve, as opposed to the equation of the straight line, as shown in the inset of Fig. **7**. This demonstrates that it is possible to derive new rate coefficients providing that there is a consistent relationship between VOC depletion factor and rate coefficient. In this way, using the curve, rate coefficients for a further 5 compounds with large depletions ($k > 30 \times 10^{-12}$) are estimated.

For the OH + monoterpene reactions, the rate coefficients determined in this work for **Mixture 3** are in good agreement with rate coefficients derived by others at this temperature, within experimental errors and literature uncertainty. This demonstrates that this type of experiment is capable of assessing the temperature dependence of VOC + OH rate coefficients. ~~The 323 K rate coefficients for the OH + alkene reactions consistently show a non-Arrhenius temperature dependence when compared with their room temperature counterparts.~~ With the exception of 1-heptene, most of the estimated coefficients for OH + alkene reactions at 323 K are within 20% of the 298 K literature values; 1-heptene displays an anomalously low result. This reflects the ~~non-Arrhenius~~temperature dependent relationship described and observed in the literature for OH addition to alkenes and monoterpenes (Chuong et al., 2002; Kim et al., 2011).

Rate~~The rate~~ coefficients for ~~OH + branched alkanes show a positive temperature dependence, which contrasts with~~ the ~~straight-~~reaction between OH and ~~cyclic alkanes~~12 aromatic VOC at 323 K are also estimated for the first time. We are also able to derive 323 K rate coefficients for the reaction between OH and three alkanes (2-methylheptane, 3-methylheptane and ethylcyclohexane) for which we could find no ~~298 K~~room temperature data in the literature~~.~~ at

~~Rate coefficients for~~ the ~~reaction between OH and 12 aromatic VOC at 323 K are also estimated for the first~~ time~~. There appears to be little to no correlation with temperature; some estimates are lower and some higher than the 298 K literature values. 3-ethyltoluene is a possible anomaly in the series, with a 323 K rate coefficient almost twice that~~ of ~~the 298 K literature measurement.~~writing. This~~, however,~~ highlights the pressing need for relevant temperature dependent rate coefficient data.

3.3 Determination of rate coefficients by ambient air sampling

The use of synthetic gas mixtures places a limitation on the complexity of mixtures that can be introduced into the reactor and can only include compounds for which authentic standards or ~~pure~~ raw materials are available. The atmosphere represents an upper limit of mixture complexity, with regards to the VOC matrix, with the added benefit of containing VOCs which may not be readily available or readily synthesised, such as secondary or tertiary oxidation products. Should the determination of rate coefficients through ambient atmospheric sampling be possible, comprehensive measurements of atmospherically relevant VOC + OH reactions could be made.

Unfortunately, there are practical challenges associated with real atmospheric air sampling. First, the complexity of the atmosphere itself poses a problem and, whilst a mass spectrometer may aid with the identification of VOCs, single column gas chromatography may not always be enough to fully resolve all of the many individual compounds observed. The presence of additional oxidants and nitrogen oxides (NO_x) may also lead to further complications and interfere with the ~~VOCs~~VOCs' concentrations during sampling and measurement. Many VOCs also exist in the atmosphere in concentrations that are orders of magnitude lower than those used in the synthetic gas mixtures outlined above, meaning that detection may be a problem, particularly after depletion using synthetic oxidants. ~~There is also likely to be a large variety in the concentrations at which atmospheric VOCs exist, which could have an adverse effect on the uniformity of individual VOC exposure to OH.~~ Finally, the atmosphere is a dynamic mixture; the components and their concentrations are subject to constant change and as such, the experimental technique would need to account for these, often rapid, temporal fluctuations.

Some of these issues can be overcome by using a dual reactor ~~instrumental~~instrument set up, allowing for two ambient air samples to be sampled simultaneously, as shown in Fig. 9. If OH is absent in both reactors then identical samples should be observed. However, in practice, it is impossible to obtain two completely indistinguishable VOC measurements due to random but minor variations in sampling and later analysis. However, comparisons between the two reactors over time can be established to account for any systematic differences that are observed between the two systems.

OH initiated reactions can be induced in one of the reactors whilst the other is sampled simultaneously in the absence of synthetic oxidants. This allows for the construction of a dataset of VOC concentrations with and without synthetic OH radicals present. Unlike for synthetic mixtures, where VOC concentrations from multiple samples were averaged before processing using Eq. (3), the natural variability in atmospheric VOC mixing ratios dictates that a $\ln\left(\frac{[\mathrm{VOC}]_0}{[\mathrm{VOC}]}\right)$ value must be calculated for each VOC for each dual sample.

Using this experimental technique for ambient air analysis, VOC reactivity was analysed at the Wolfson Atmospheric Chemistry Laboratories at the University of York, a suburban site in York, United Kingdom during the period 6th -10th June 2014. The sampling site was approximately 200 m from a local commuter road, 1.5 km from a dual carriageway and in close proximity to a small area of woodland consisting primarily of oak and sycamore trees. There was a large dynamic range in the concentrations of VOC observed; some species, for instance styrene, experienced large degrees of scatter, due in part to very low ambient mixing ratios (16 parts per trillion by volume (pptv)). 5 ppb of ozone was also detected at the end of the ~~reactor~~reactors. This could be attributed to the presence of non-synthetic oxidants and NO_x, but is likely to be the ambient ozone sampled from outside that made it through the heated sample lines. At this concentration, given the rate of reaction between O_3 and all the compounds analysed, it is unlikely that the O_3 would have a significant impact on the degradation of any species within the reactor. Indeed, even for the reaction between O_3 and styrene, which proceeds at 1.70×10^{-17} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003), the depletion by O_3 accounts for less than one per cent of its total depletion (see Supplementary Information Table S2).

23 VOCs (including alkanes, alkenes, aromatics, isoprene, monoterpenes, naphthalene, ethyl acetate, dichloromethane – see Table 4) were positively identified from the GC-MS data. The vast majority of identified VOCs have very slow rate coefficients for reaction with O_3, with a maximum of 1×10^{-20} cm^3 $molecule^{-1}$ s^{-1} for the alkanes and alkylbenzenes (Atkinson and Arey, 2003). Of the 23 identified compounds, four monoterpenes (α-pinene, β-pinene, 3-carene and limonene) react relatively fast with both OH and O_3 (see Table 4) and their concentrations were decreased to below the limit of detection for the "lamp on" samples. These four compounds were therefore removed from subsequent analyses.

~~Depletions~~Depletion factors for the eight identified compounds which have 323 K literature rate coefficients are shown in Fig. 10 in blue. There is a clear linear relationship, shown by the black dashed line, between the depletion ~~in~~factors for these eight compounds and their rate ~~of~~coefficient for reaction with OH. However, a significant section of the plot lacks literature data for comparison. ~~To~~It may therefore be beneficial, in future work deriving rate coefficients from real air samples, to synthetically spike the air with a range of reference compounds whose rate coefficients are accurately known, in order to ensure that the best possible correlation between depletion factor and literature rate coefficient can be generated across the desired range. In the absence of this, and to aid in the clarification of the linear relationship between rate coefficient and depletion factor, seven compounds, whose rate coefficients were derived in earlier studies using synthetic gas mixtures (**Mixture 3**) are also plotted in yellow. Six of these compounds are in good agreement with the linear correlation derived using the literature, within experimental error. A linear fit to the 323 K data which excludes isoprene, the fasting reacting observed VOC, is shown by the red dashed line. This linear regression gives a slightly better fit to the data derived from the synthetic gas mixture.

The relative rate results for 19 compounds are provided in Table 4. Except for n-hexane and dichloromethane, the 323 K rate coefficients for six compounds (benzene, isoprene, *n*-heptane, *n*-decane, naphthalene and toluene) are in reasonable agreement to comparable rate coefficients in the literature. Two compounds (dichloromethane and ethyl acetate) yield negative rate coefficients as the depletions in their concentrations were generally smaller than the instrument noise. New rate coefficients, at 323 K, for three compounds (dodecane, styrene and tridecane) are also derived for the first time.

The ambient air derived rate coefficient for the OH + 3-ethyltoluene reaction is almost twice as large as that determined using the synthetic mixture, which itself was anomalously larger than the 298 K literature equivalent. Many *k* values determined using ambient air sampling are systematically larger than those in the literature for reactions at 298 K. This is likely due to the increased complexity of sampling and analysing ambient air when compared with synthetic gas mixtures (as discussed above) and the large range in terms of both reactivity and concentration in the compounds sampled.

However, it is clearly still possible to estimate reasonable rate coefficients, albeit with higher uncertainties, for most of the ambient observed compounds. The use of this technique is therefore especially useful for VOCs which are not commercially available or easily synthesised or isolated, such as the oxidation products of common atmospheric species.

4 Atmospheric implications and conclusions

We have demonstrated here a simple and versatile method for measuring relative rate coefficients for reactions of OH with multiple VOCs simultaneously, ~~using~~based upon the the well-established relative rate kinetic technique~~ as a basis~~. The method builds upon that used to estimate the contribution of unidentified VOCs to OH reactivity (Kato et al., 2011). Three synthetic gas mixtures have been used with this technique, covering a broad range in VOC functionality and in rates of reaction with OH radicals. Additionally, these mixtures have been studied at different temperatures, showing that this method could be applied to quickly generate temperature dependant Arrhenius expressions for multiple VOCs with only very simple, minor modifications to the current set up. Consequently, we have been able to estimate novel rate coefficients at 323 K for a total of 28 atmospherically relevant VOCs, including three that have no measurements at ~~298 K~~room temperature (2-methylheptane, 3-methylheptane and ethylcyclohexane). We have also been able to provide results which are in good agreement with the only previously recorded measurements for the reactions between OH and γ-terpinene and OH and cycloheptene, along with various other VOCs for which few results were previously available.

We have shown that this method can produce ~~novel results~~rate coefficients for VOCs, the OH kinetics of which have not been investigated to date by providing the first measurement of the OH + 2,3-dimethylpent-1-ene reaction, at room temperature, of $k = 5.7\ (\pm\ 0.3) \times 10^{-11}$ cm^{3} molecule^{-1} s^{-1}. Using an approximate atmospheric concentration of OH, of 1×10^{6} molecules cm^{-3}, this gives an estimated OH lifetime for 2,3-dimethylpent-1-ene of 4.9 hours. This corresponds to 2.5 times its loss rate with respect to O_3 (estimated using an approximate atmospheric O_3 concentration of 30 ppb and the SAR provided in King et al. (1999)).

We have also shown that using a dual-reactor set up allows for the derivation of rate coefficients via ambient air sampling. Rate coefficients for six compounds were shown to be in reasonable agreement with the literature. Additionally, a further three new rate coefficients were measured at 323 K using this method of ambient air sampling (dodecane, styrene and tridecane). Further improvements in analytical detection limits and chromatographic resolution would allow the method to be extended to more ~~VOC~~VOCs, including less volatile organics. By using a TOF-MS, there is also the possibility of retrospectively determining OH + VOC reaction rates, should a species be deemed important in the future.

In summary, this technique represents a significant breakthrough in the measurement of atmospherically relevant oxidation kinetics. The throughput of target compounds has been improved dramatically with respect to the base relative rate technique, which will allow for the rapid development of experimentally derived measurements for homologous series of multifunctional, long chain and branched systems, as demonstrated by that for the 1-alkenes in this work. The possibility of conducting temperature dependent studies will allow for a significant broadening of our knowledge in this area. The technique could also be adapted for use with Cl or NO_3 radicals, for which oxidative kinetic measurements are severely limited in the literature. Additionally, the use of ambient air with this technique demonstrates its versatility, and highlights the possibility of measuring reaction rates for difficult~~–~~-to~~–~~-synthesise, or currently unidentified, VOCs. Finally, the rate coefficients for reactions of OH with unidentified VOCs in the atmosphere can be measured using this method. If the concentrations of these species can be estimated, then the method would enable missing OH reactivity to be quantified.

Data availability

Raw data is available upon request.

Author contribution

ACL, ARR, DEH, JFH & LKW planned the overall project; DEH, LJC, JFH & TJD designed experiments; DRC, GAB, LKW, NR, RED & TI conducted initial experiments; JTS~~ &~~, RTL & FCW conducted later experiments; JTS & RTL performed the analysis; JTS, RTL & 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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Table 1 Results of relative rate experiments, with literature data, for each VOC in Mixture 1, ordered by measured *k* value.

Compound	**Range of depletion / %**	**Measured *k* (295 K)[a] / 10^{-12} cm^3 molecule^{-1} s^{-1}**	**Evaluated literature *k* (298 K) / 10^{-12} cm^3 molecule^{-1} s^{-1}**	**Reference[b]**	**Number of literature measurements**
β-ocimene	27-70	~~222 ± 7~~223 ± 10	245 ± 49[c]	Atkinson and Arey, 2003	4
γ-terpinene	24-63	~~206~~207 ± 6	170 $\left(^{+44}_{-35}\right)$	Atkinson et al., 2006[d]	1
myrcene	24-62	204 ± ~~7~~8	209 ± 42[c]	Atkinson and Arey, 2003	4
limonene	18-57	152 ± 4	170 ± 51	Atkinson and Arey, 2003	5
isoprene	12-41	104 ± 6	100 $\left(^{+15}_{-13}\right)$	Atkinson et al., 2006[d]	25+
3-carene	11-40	97 ± ~~3~~4	85 ± 17[c]	Atkinson and Arey, 2003	2
β-pinene	9-34	~~76 ± 9~~78 ± 11	79 ± 20	Atkinson and Arey, 2003	10
α-pinene	7-24	56 ± 6	53 $\left(^{+22}_{-15}\right)$	Atkinson et al., 2006[d]	9
m-xylene	3-13	~~21~~22 ± 6	23 ± 4	Atkinson and Arey, 2003	15
o-xylene	2-7	~~1.6 ± 1.0~~4.8 ± 7	13 ± 3	Atkinson and Arey, 2003	10

[a] errors are likely underestimated as they do not include the large uncertainties in the literature rate coefficients used as reference compounds.

[b] data from Atkinson and Arey (2003) is collated from multiple sources including Calvert et al. (2000, 2002).

[c] original result relative to 2,3-dimethylbut-2-ene; $k = 1.13 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Updated result relative to $k = 1.1\ (\pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} as recommended in Calvert et al. (2002).

[d] see also IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation Website – ~~http://iupac.pole-ether.fr~~**http://iupac.pole-ether.fr**

Table 2 Results of relative rate experiments, with literature data, for each VOC in Mixture 2, ordered by measured *k* value.

Compound	Range of depletion / %	Measured *k* (295 K)[a] / 10^{-12} cm^3 molecule^{-1} s^{-1}	Evaluated literature *k* (298 K) / 10^{-12} cm^3 molecule^{-1} s^{-1}	Reference[b]	Number of literature measurements
isoprene	8-26	~~101 ± 4~~103 ± 5	100 ($^{+15}_{-13}$)	Atkinson et al., 2006[d]	25+
β-pinene	5-21	~~74~~75 ± 12	79 ± 20	Atkinson and Arey, 2003	10
cycloheptene	6-20	74 ± ~~9~~10	74 ± 10[c]	Atkinson and Arey, 2003	1
cyclohexene	6-20	71 ± 4	68 ± 17	Atkinson and Arey, 2003	9
cyclopentene	7-19	~~67 ± 8~~69 ± 9	67 ± 23	Atkinson and Arey, 2003	3
2,3-dimethylpent-1-ene	5-17	57 ± 3			
α-pinene	4-17	53 ± 4	53 ($^{+22}_{-15}$)	Atkinson et al., 2006[d]	9
1-octene	4-15	~~43~~44 ± 5	41.4 ± 0.8	Aschmann and Atkinson, 2008	2
1-nonene	4-15	~~42~~41 ± 3	43.2 ± 0.5	Aschmann and Atkinson, 2008	2
1-heptene	3-13	~~35 ± 3~~36 ± 4	40 ± 12	Atkinson and Arey, 2003	2
1-hexene	2-15	~~29 ± 21~~46 ± 12	37 ± 11	Atkinson and Arey, 2003	2

[a] errors are likely underestimated as they do not include the large uncertainties in the literature rate coefficients used as reference compounds.

[b] data from Atkinson and Arey (2003) is collated from multiple sources including Calvert et al. (2000, 2002).

[c] original result relative to isoprene; $k = 1.01 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Updated result relative to $k = 1.00$ ($^{+0.15}_{-0.13}$) $\times 10^{-10}$ cm^3 molecule^{-1} s^{-1} as recommended by Atkinson et al. (2006)§.

[d] see also IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation website – ~~http://iupac.pole-ether.fr~~**http://iupac.pole-ether.fr**

Table 3 Results of relative rate experiments, with literature data, for each VOC in Mixture 3, ordered by curve measured *k* value.

Group	Compound	p_0[a] / mmHg	Estimated cylinder concentration / ppb	Linear measured *k* (323 K) / 10^{-12} cm^{3} molecule^{-1} s^{-1}	Curve measured *k* (323 K) / 10^{-12} cm^{3} molecule^{-1} s^{-1}	Literature *k* / 10^{-12} cm^{3} molecule^{-1} s^{-1} 323 K	Evaluated literature *k* / 10^{-12} cm^{3} molecule^{-1} s^{-1} 298 K
Biogenics	β-ocimene	1.60	0.23		950 ± 800	261 $(^{+54}_{-48})^{e}$	245 ± 49^{b}
	myrcene	2.09	0.31		310 ± 105	253 $(^{+68}_{-56})^{d}$	209 ± 42^{b}
	γ-terpinene	1.10	0.16		180 ± 19		170 $(^{+44}_{-35})^{c}$
	limonene	1.98	0.29		140 ± 5	148 $(^{+21}_{-18})^{b}$	170 ± 51^{b}
	3-carene	1.90	0.28		81 ± 1~~.5~~		85 ± 17^{b}
	β-pinene	2.93	0.43		81 ± 20	66 $(^{+11}_{-9.4})$~~^{1}~~^{b}	79 ± ~~20^{1}~~20^{b}
	isoprene	550	80.4		75 ± 8	90 $(^{+33}_{-24})$~~^{2}~~^{c}	100 $(^{+15}_{-13})$~~^{2}~~^{c}
	α-pinene	4.75	0.69	48 ± ~~3~~4	50 ± 2	47 $(^{+8.3}_{-7.0})$~~^{2}~~^{c}	53 $(^{+22}_{-15})$~~^{2}~~^{c}
	camphene	2.50	0.37	47 ± 3	50 ± 2		53 ± ~~7^{1}~~7^{b}
Alkenes	cycloheptene	22.5	3.29		71 ± 4		74 ± 10^{b}
	cyclopentene	378	55.3	~~52 ± 2~~53 ± 3	58 ± ~~0.9~~1		67 ± ~~23^{1}~~23^{b}
	cyclohexene	89.0	13.0	~~52~~53 ± 5	57 ± 4		68 ± 17^{b}
	1-hexene	184	26.9	~~32~~33 ± 6	31 ± 5		37 ± ~~11^{1}~~11^{b}
	1-heptene	59.3	8.67	~~17~~18 ± 2	18 ± 1~~.2~~		40 ± 12^{b}
Alkanes	cyclooctane	4.60	0.67	17 ± ~~0.8~~1	17.4 ± 0.5	15 $(^{+8}_{-5})^{b}$	13 ± 0.4^{b}
	cycloheptane	21.6	3.16	14 ± 2	15 ± 1~~.2~~	13 $(^{+6}_{-4})^{b}$	12 ± 3^{b}
	ethylcyclohexane	31.0	4.54	15 ± 1~~.0~~	15 ± ~~0.5~~1		
	3-methylheptane	19.6	2.87	~~12~~13 ± 3	14 ± 2		
	n-decane	1.43	0.21	13 ± ~~3~~2	14 ± 1~~.5~~	12 $(^{+2}_{-1.9})^{b}$	11 ± 2^{b}
	n-nonane	4.45	0.65	14 ± ~~1.4~~2	14 ± ~~0.7~~1	10 $(^{+1.1}_{-1.0})^{b}$	10 ± 1.9^{b}
	2-methylheptane	20.5	3.00	12 ± ~~0.2~~1	12.2 ± 0.2		

	2-methylpentane	211	30.8	~~10~~11 ± 3	12 ± 2		5.2 ± 1.~~3^1~~3^b
	3-methylpentane	190	27.8	8.~~4~~7 ± 1.~~2~~1	9.1 ± 0.9		5.2 ± 1.~~3^1~~3^b
	n-octane	14.1	2.06	~~6~~7.8 ± ~~2~~1.8	8.8 ± 1.4	8.7 $(^{+2}_{-1.7})$~~^{1}~~^{b}	8.1 ± 1.~~6^1~~6^b
	n-heptane	46.0	6.73	8.~~1~~3 ± 0.8	7.9 ± 0.5	7.2 $(^{+2}_{-1.6})$~~^{1}~~^{b}	6.8 ± 1.~~4^1~~4^b
	2,2,3-trimethylbutane	90.0	13.2	~~3.8~~4.6 ± 1.~~2~~9	6.3 ± 2.0	4.0 $(^{+1.7}_{-1.2})$~~^{1}~~^{b}	3.8 ± 1.~~0^1~~0^b
Aromatics	3-ethyltoluene	3.00	0.44	34 ± ~~0.9~~1	34 ± ~~0.6~~1		19 ± 7^b
	1,2,4-trimethylbenzene	2.10	0.31	32 ± ~~1.5~~2	32 ± 1~~.0~~		33 ± 8^b
	1,2,3-trimethylbenzene	1.69	0.25	~~31~~32 ± 1~~.2~~	31 ± ~~0.9~~1		33 ± 8^b
	naphthalene	0.085	0.01	22 ± 1~~.4~~	22 ± 1~~.2~~	22.4^b	23 ± 6^b
	m-xylene	8.29	1.21	21 ± ~~1.5~~2	21 ± 1~~.3~~		23 ± ~~4^1~~4^b
	indane	1.50	0.22	19 ± ~~0.6~~1	19 ± ~~0.6~~1		19 ± 8^b
	4-ethyltoluene	2.90	0.42	16 ± ~~0.4~~1	~~16~~15.6 ± 0.~~14~~1		12 ± 4^b
	2-ethyltoluene	2.60	0.38	15 ± 1~~.0~~	15 ± ~~0.5~~1		12 ± 4^b
	o-xylene	6.61	0.97	12 ± 1~~.0~~	13 ± ~~0.6~~1		13 ± ~~3^1~~3^b
	4-isopropyltoluene	1.50	0.22	12 ± 1~~.2~~	12 ± ~~0.9~~1		14 ± 3^{b,f}
	n-propylbenzene	4.50	0.66	8.~~5~~6 ± 0.~~7~~9	8.5 ± 0.5		5.8 ± 1.~~5^1~~5^b
	isopropylbenzene	4.50	0.66	~~5.~~6.2 ± 1.5	7.2 ± 1.0		6.3 ± ~~2^1~~2^b
	ethylbenzene	9.60	1.40	~~5.7~~6.2 ± 1.3	7.0 ± 1.0		7.0 ± ~~2^1~~2^b
	toluene	28.4	4.15	~~4.9 ±~~ 5.0~~.6~~ ± 0.5	5.1 ± 0.3	5.2 $(^{+4}_{-2})$~~^{2}~~^{c}	5.6 $(^{+1.5}_{-1.2})$~~^{2}~~^{c}

[a] p_0 refers to the vapour pressure of the VOC. This was used to estimate the concentration of VOC transferred to the cylinder.

[b] Atkinson and Arey, 2003

[c] Atkinson et al., 2006 (see also IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation website – http://iupac.pole-ether.fr)

[d] Hites and Turner, 2009

[e] Kim et al., 2011

[f] original result relative to cyclohexane; *k* = 7.14 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Updated result relative to *k* = 6.97 (± 1.4) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} as recommended by Atkinson and Arey (2003).

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Table 4 Results of relative rate experiments, with literature data, for VOC in the ambient air analysis, ordered by ambient air measured *k* value.

compound	**ambient air measured *k* (323 K) / 10^{-12} cm^{3} molecule^{-1} s^{-1}**	**synthetic mixture measured *k* (323 K) / 10^{-12} cm^{3} molecule^{-1} s^{-1}**	**literature *k* (323 K) / 10^{-12} cm^{3} molecule^{-1} s^{-1}**	**literature *k* (298 K) / 10^{-12} cm^{3} molecule^{-1} s^{-1}**
tridecane	140 ± 10			15.1 ± 3.8^{a}
isoprene	90 ± 3	75 ± 8	90 $\left(^{+\,33}_{-\,24}\right)^{b}$	100 $\left(^{+\,15}_{-\,13}\right)^{b}$
styrene	81 ± 7			58 ± 12^{a}
3-ethyltoluene	70 ± 5	34 ± ~~0.6~~1		19 ± 7^{a}
dodecane	58 ± 8			13 ± 3^{a}
1,2,3-trimethylbenzene	44 ± 4	31 ± ~~0.9~~1		33 ± 8^{a}
1,2,4-trimethylbenzene	40 ± 4	32 ± 1~~.0~~		33 ± 8^{a}
naphthalene	29 ± 5	22 ± 1~~.2~~	22.4^{a}	23 ± 6^{a}
2-ethyltoluene	24 ± 3	15 ± ~~0.5~~1		12 ± 4^{a}
n-decane	20 ± 3	14 ± 1~~.5~~	12 $\left(^{+\,2}_{-\,1.9}\right)^{a}$	11 ± 2^{a}
ethylbenzene	16 ± 2	7.0 ± 1~~.0~~		7.0 ± 2^{a}
n-heptane	9.3 ± 2.2	7.9 ± 0.5	7.2 $\left(^{+\,2}_{-\,1.6}\right)^{a}$	6.8 ± 1.4^{a}
n-propylbenzene	7.4 ± 3.0	8.5 ± 0.5		5.8 ± 1.5^{a}
toluene	5.4 ± 1.2	5.1 ± 0.3	5.2 $\left(^{+\,4}_{-\,2}\right)^{a}$	5.6 $\left(^{+\,1.5}_{-\,1.2}\right)^{b}$
benzene	3.6 ± 1.1		1.3 ± 0.4^{a}	1.2 ± 0.2^{a}
isopropylbenzene	1.8 ± 0.8	7.2 ± 1.0		5.8 ± 1.2^{a}
n-hexane	0.~~86~~9 ± 0.5		5.8 ± 0.5^{a}	5.2 ± 1.3^{a}
ethyl acetate	-0.13 ± 0.04			1.7 ± 0.3^{c}
dichloromethane	-1.5 ± 0.9		0.13 $\left(^{+\,0.07}_{-\,0.05}\right)^{b}$	0.1 $\left(^{+\,0.03}_{-\,0.02}\right)^{b}$

[a] Atkinson and Arey, 2003

[b] Atkinson et al., 2006 (see also IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation website – http://iupac.pole-ether.fr)

[c] Calvert et al., 2011

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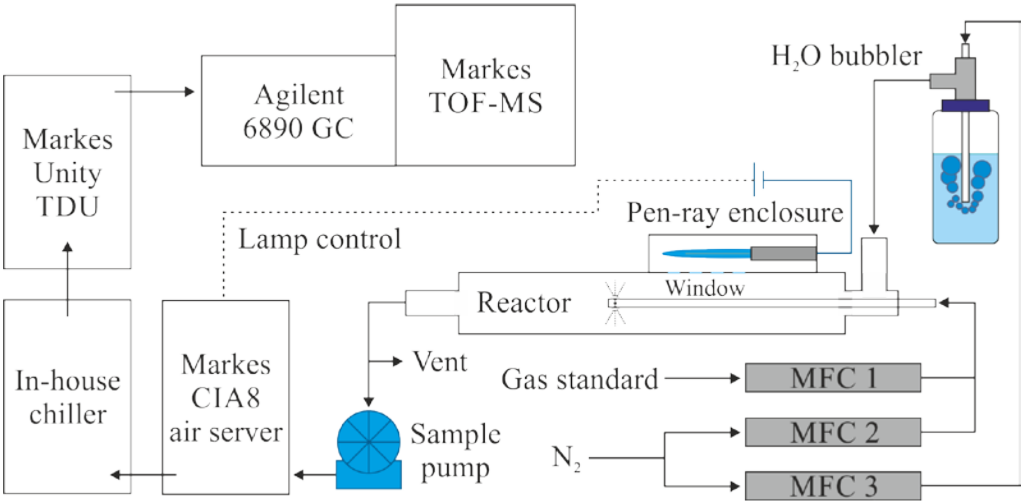

Figure 1 Schematic of the OH reactor configuration used. Key to abbreviations: CIA8 = air server and canister interface accessory; GC = gas chromatograph; MFC = mass flow controller; TOF-MS = time of flight mass spectrometer; TDU = thermal desorption unit. The flow rate through MFC 1 was stepped from 200 sccm through to 1000 sccm in 200 sccm intervals. The combined flow rate through MFC 1 and MFC 2 was kept constant at 1000 sccm. The flow rate through MFC 3, and hence through the H_2O bubbler, was set to 2000 sccm resulting in a total flow through the reactor of 3000 sccm. The residence time of VOC inside the reactor after injection was approximately 4 s, with the oxidation chemistry expected to occur in under 0.5 s.

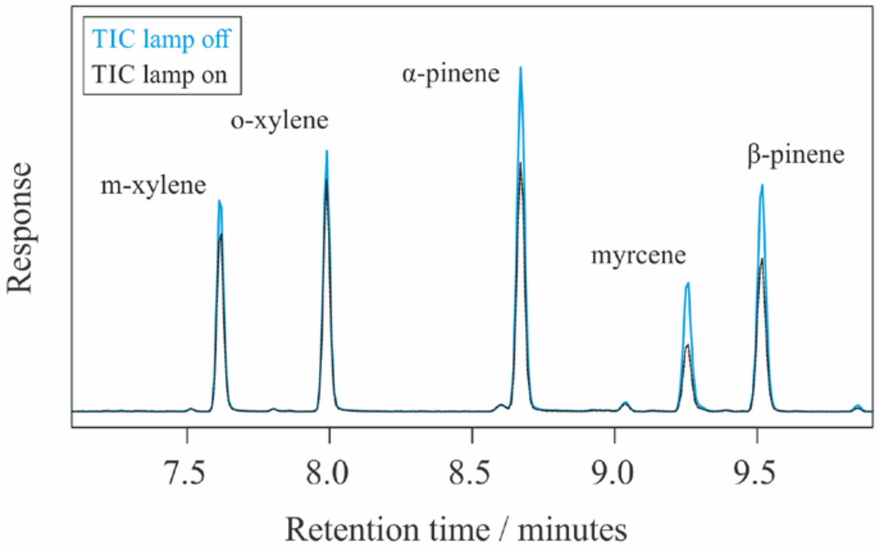

Figure 2 Typical total ion chromatograms (TICs) obtained for a ppbv mixing ratio gas standard (Mixture 1) with the lamp off (~~black~~blue) and lamp on (~~blue~~black). Greater differences in peak areas are observed for VOC which react faster with OH. Literature rate coefficients (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) for the VOC are *m*-xylene[1], 23 (± 4); *o*-xylene[1], (13 ± 3); α-pinene[2], (53^{+22}_{-15}); myrcene[1], 209 ± (42) and β-pinene[1], 79 ± (20).

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[1] Atkinson and Arey (2003) updated to reflect changes in reference compound

[2] Atkinson et al. (2006) – http://iupac.pole-ether.fr/

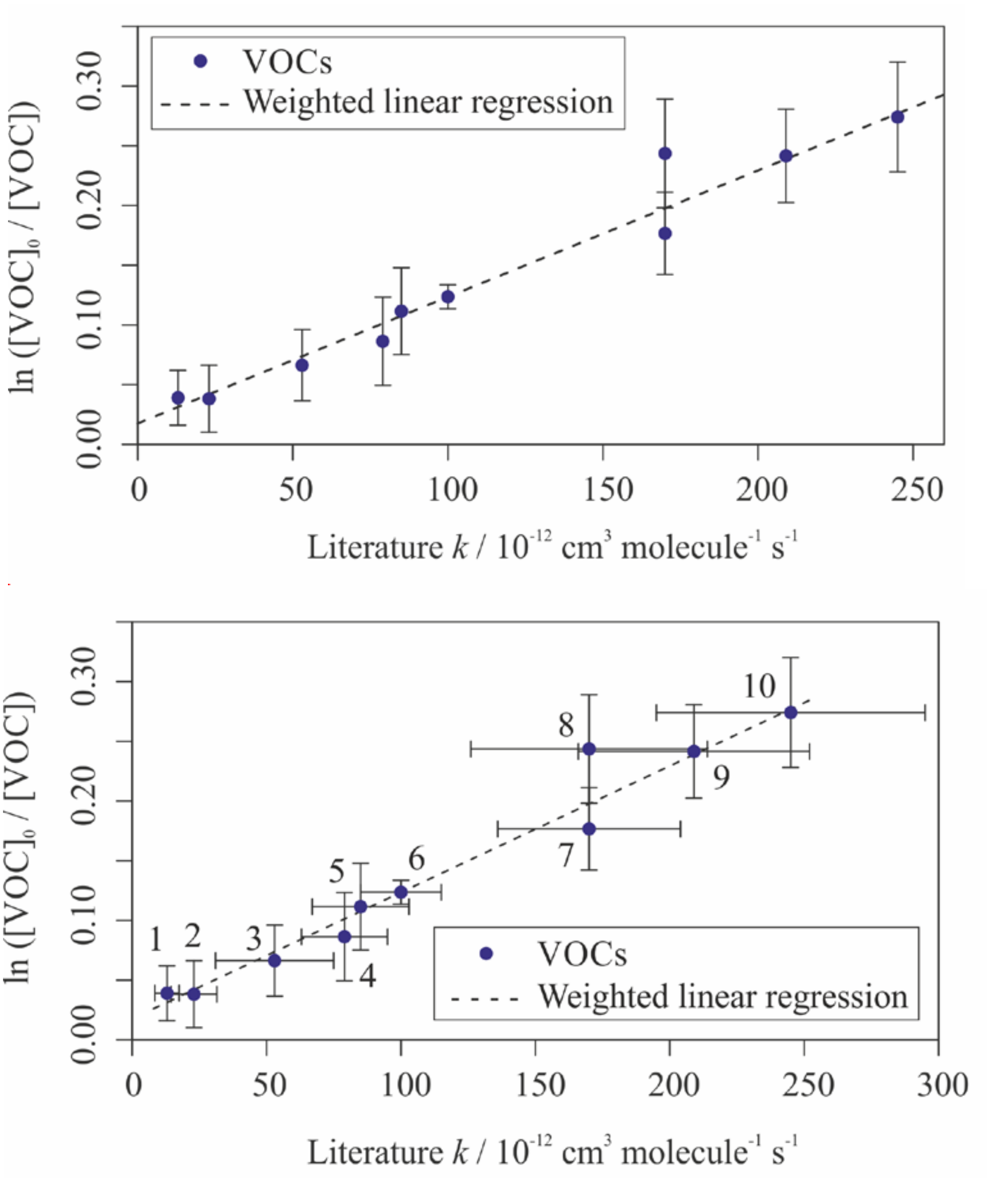
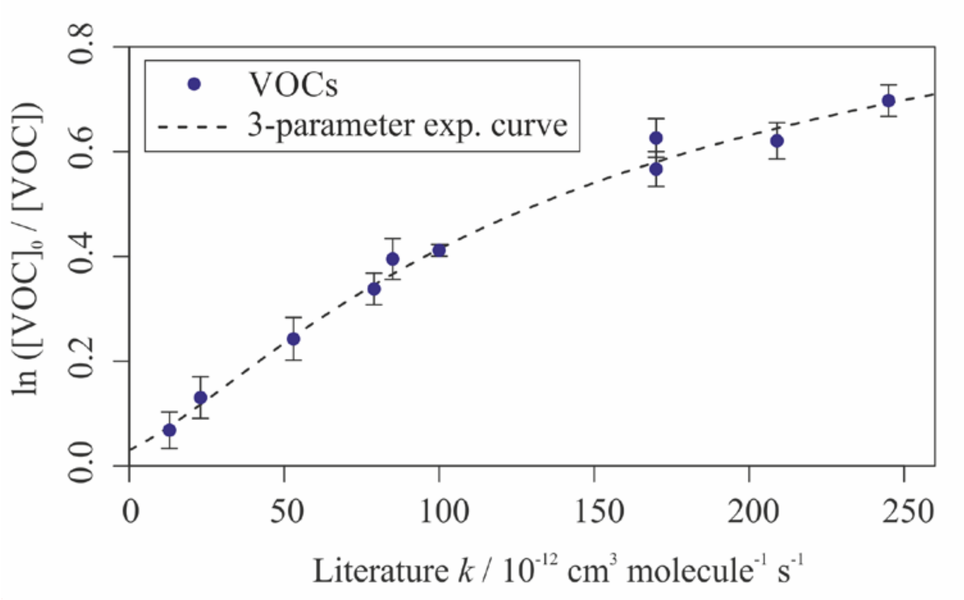


Figure 3 Relative rate plot for Mixture 1 (OH reactivity = 240 s^{-1}) at 295 K. Compounds with a known rate coefficient are plotted using literature values. Error bars on the y-axis, equal to one standard error, are calculated by combining the standard error in

peak areas for 6 lamp off samples and 6 lamp on samples. Error bars on the x-axis ~~are not displayed as they~~ are typically large (approximately ± 20-30%) and account for deviations from the line. A weighted (to the uncertainty in the y-values) linear fit was used to generate the slope with a value of OH_{exp} = 1.1 (± 0.07) × 10^9 molecules cm^{-3} s and R^2 of 0.96. Identity of VOCs: 1, *o*-xylene; 2, *m*-xylene; 3, α-pinene; 4, β-pinene; 5, 3-carene; 6, isoprene; 7, limonene; 8, γ-terpinene; 9, myrcene; 10, β-ocimene.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ln ([VOC]$_0$ / [VOC])
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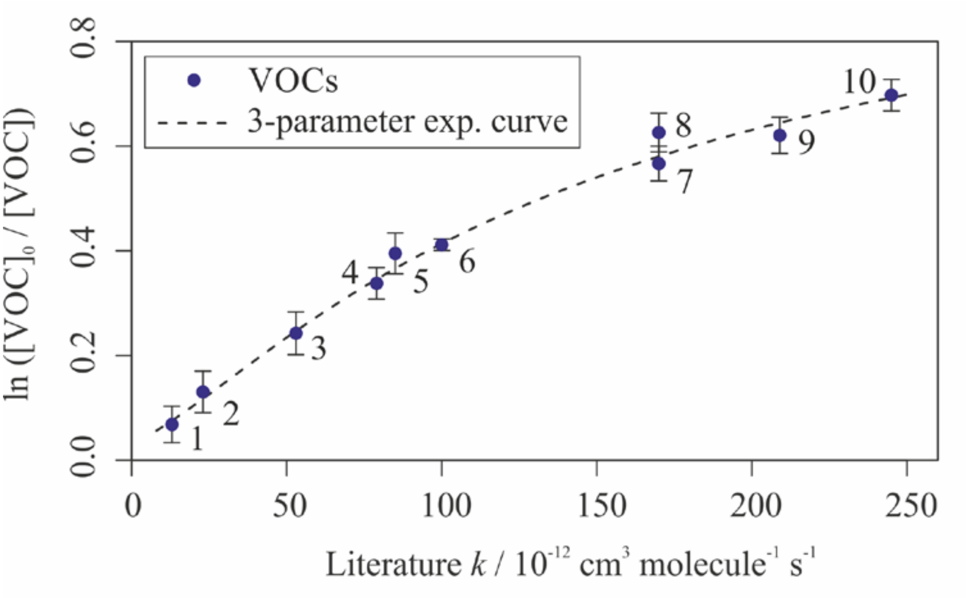
VOCs
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0.4
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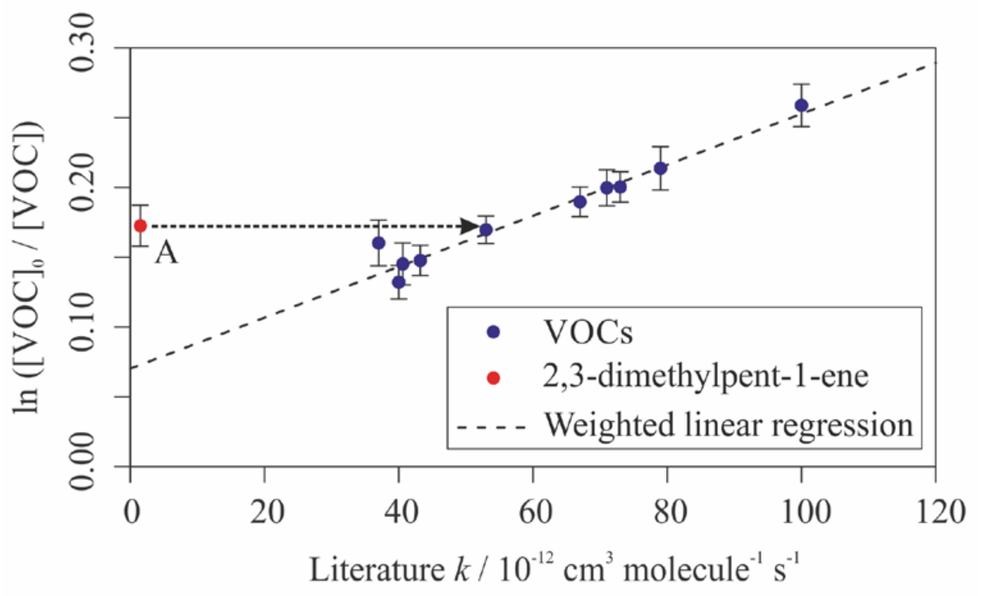
200
250
Literature k / 10^{-12} cm^3 molecule^{-1} s^{-1}

Figure 4 Relative rate plot for Mixture 1 (OH reactivity = 50 s^{-1}) at 295 K. Compounds with a known rate coefficient are plotted using literature values. Error bars on the y-axis, equal to one standard error, are calculated by combining the standard error in peak areas for 6 lamp off samples and 6 lamp on samples. Error bars on the x-axis are not displayed ~~as they~~for reasons of clarity but are typically large (approximately ± 20-30%) and account for deviations from the line. The black dashed line shows the relationship observed when VOC concentrations are low, modelled by a three-parameter exponential curve (see Supplementary Information). Identity of VOCs: 1, *o*-xylene; 2, *m*-xylene; 3, α-pinene; 4, β-pinene; 5, 3-carene; 6, isoprene; 7, limonene; 8, γ-terpinene; 9, myrcene; 10, β-ocimene.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● VOCs
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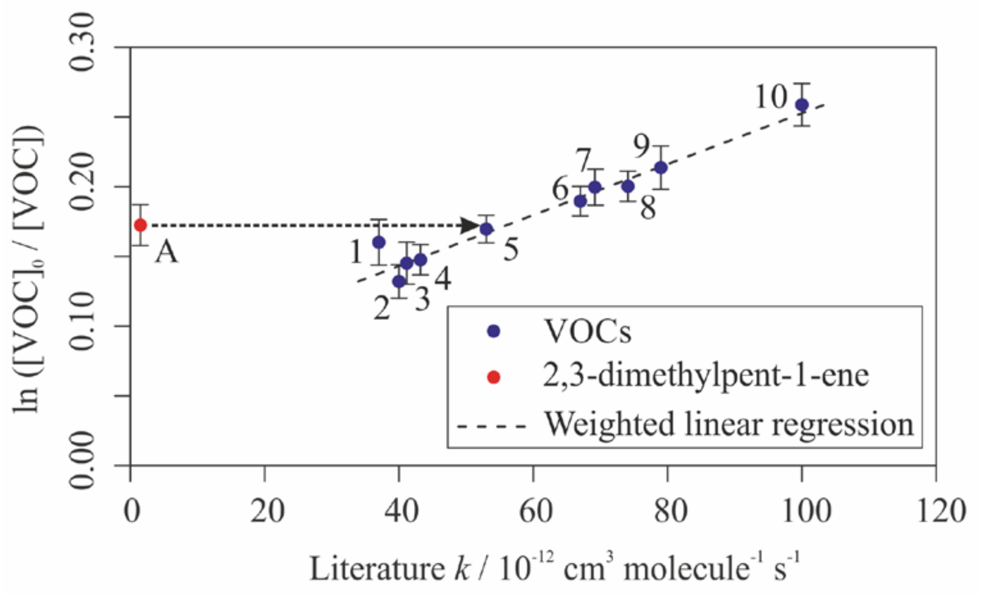
ln ([VOC]₀ / [VOC])
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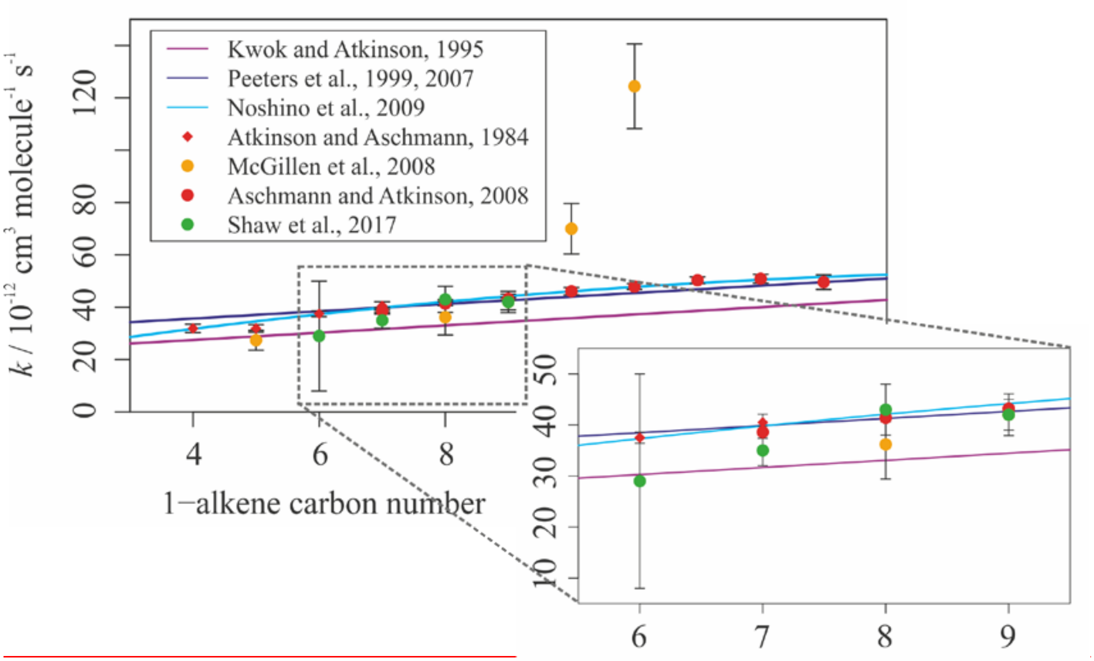
● VOCs
● 2,3-dimethylpent-1-ene
- - - - Weighted linear regression

Figure 5 Relative rate plot for Mixture 2 (OH reactivity = 30 s^{-1}) at 295 K. Compounds with a known rate coefficient are plotted using literature values. Error bars on the y-axis, equal to one standard error, are calculated by combining the standard error in peak areas for 6 lamp off samples and 6 lamp on samples. See Supplementary Information Fig. S4 for a plot displaying x-axis error bars, which are not shown here due to reasons of clarity. A weighted linear fit was used to generate the slope with a value of OH_{exp} = 1.8 (± 0.14) × 10^9 molecules cm^{-3} s and R^2 of 0.95. Data for 2,3-dimethylpent-1-ene~~,~~ (A), which has no literature *k* value, was not used in the calculation of the fit. Identity of VOCs: 1, 1-hexene; 2, 1-heptene; 3, 1-octene; 4, 1-nonene; 5, α-pinene; 6, cyclopentene; 7, cyclohexene; 8, cycloheptene; 9, β-pinene; 10, isoprene.


Kwok and Atkinson, 1995
Peeters et al., 1999, 2007
Noshino et al., 2009
Atkinson and Aschmann, 1984
McGillen et al., 2008
Aschmann and Atkinson, 2008
Shaw et al., 2017
k / 10^-12 cm^3 molecule^-1 s^-1
0
20
40
60
80
120
4
6
8
1−alkene carbon number
10
20
30
40
50
6
7
8
9

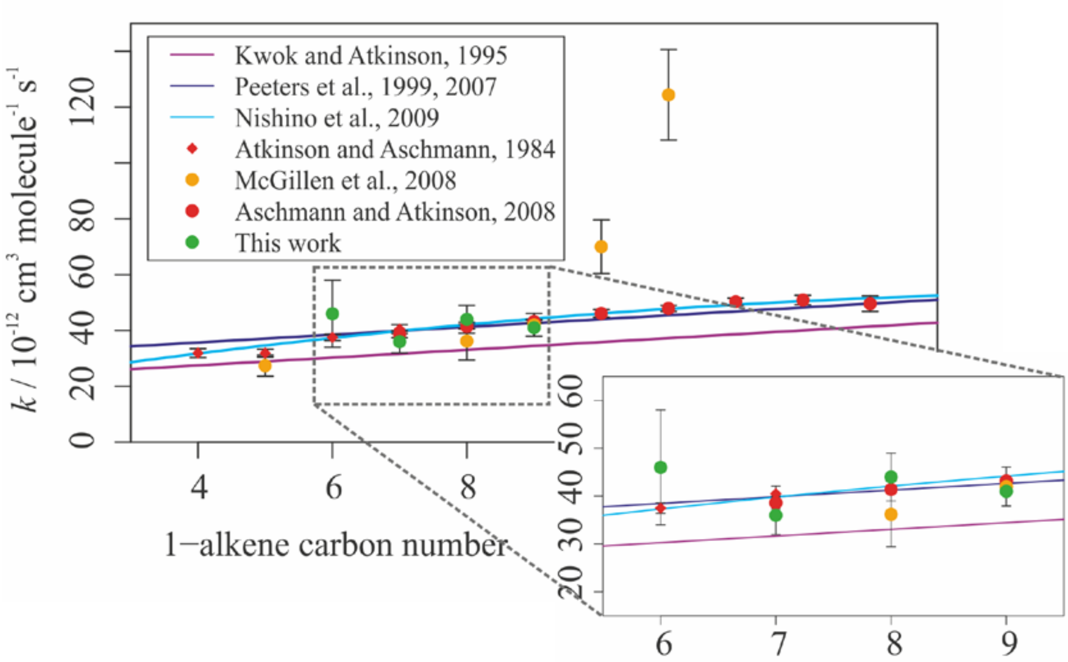
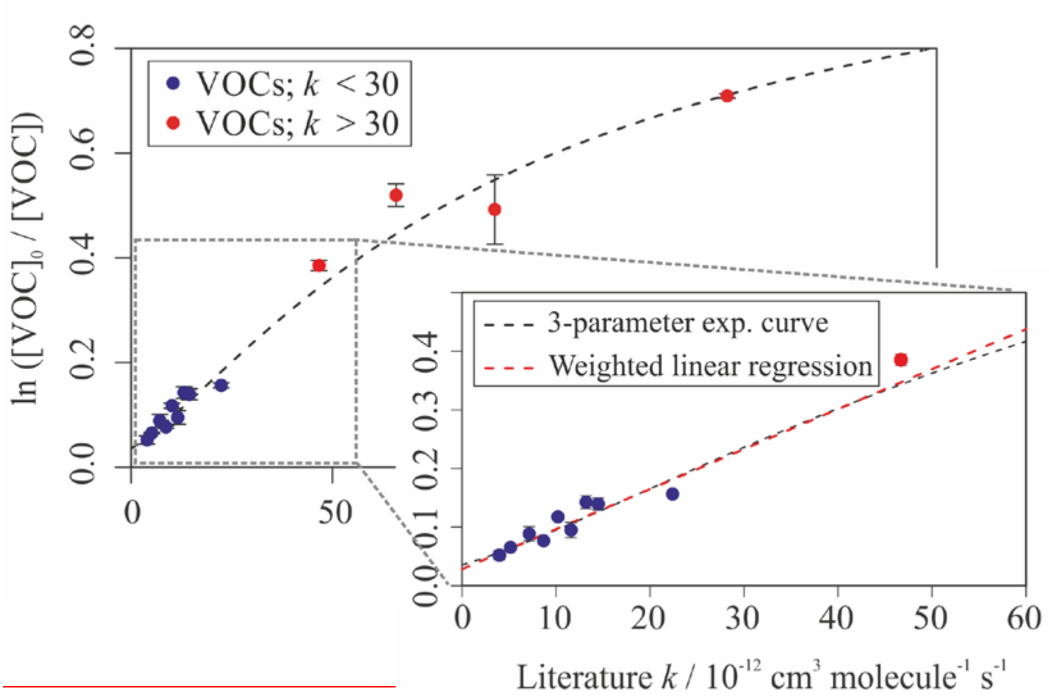


Figure 6 Plot showing experimentally derived (data points) and predicted SAR derived (lines) *k* values for 1-alkenes. Data from this study are shown in green; they are in good agreement with both previous experimentally derived results and with theoretical SARs.


ln ([VOC]$_0$ / [VOC])
0.0
0.2
0.4
0.6
0.8
0
50
● VOCs; k < 30
● VOCs; k > 30
- - - 3-parameter exp. curve
- - - Weighted linear regression
0.0
0.1
0.2
0.3
0.4
0
10
20
30
40
50
60
Literature k / 10^{-12} cm^3 molecule^{-1} s^{-1}

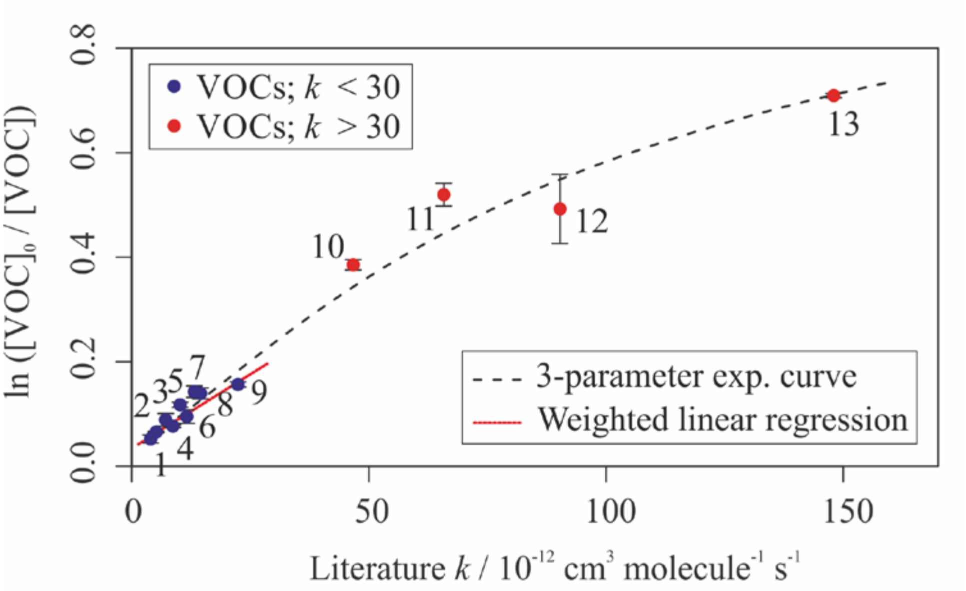


Figure 7 Relative rate plot for Mixture 3 (OH reactivity = 60 s^{-1}) at 323 K. Compounds with a known rate coefficient are plotted using literature *k* (323 K) values. Error bars on the y-axis, equal to one standard errors, are calculated by combining the standard error in peak areas for 5 lamp off samples and 5 lamp on samples. See Supplementary Information Fig. S5 for a plot displaying x-axis error bars, which are not shown here for reasons of clarity. The black dashed line shows the relationship observed when VOC concentrations are low, modelled by an exponential cumulative distribution. A weighted linear fit was used to generate the red slope (R^2 of 0.976) for VOC with *k* (323 K) less than 30 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}.

Identify of VOCs: 1, 2,2,3-trimethylbutane; 2, toluene; 3, *n*-heptane; 4, *n*-octane; 5, *n*-nonane; 6, *n*-decane; 7, cycloheptane; 8, cyclooctane; 9, naphthalene; 10, α-pinene; 11, β-pinene; 12, isoprene; 13, limonene.

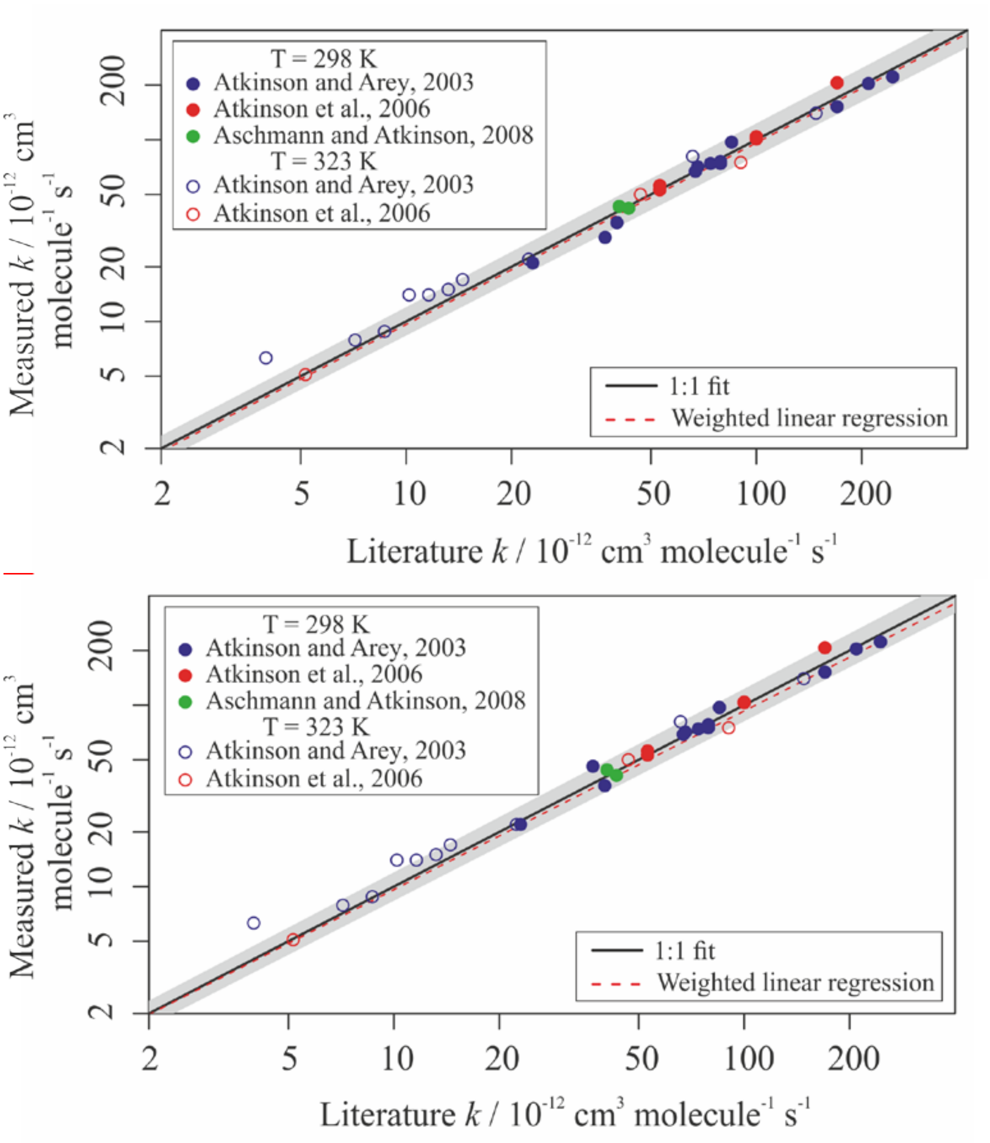


Figure 8 Measured VOC + OH rate coefficients plotted against literature VOC + OH rate coefficients for all compounds measured as part of mixtures 1, 2 and 3. Filled points represent data collected at room temperature (294 (± 2) K) and empty points represent data collected at the elevated temperature of 323 (± 10) K. The grey shaded area demonstrates a 25% uncertainty in the 1:1 gradient; most data falls well within this bound. Data lying outside this bound include: 1-hexene at room temperature and 2,2,3-

trimethylbutane~~,~~ and *n*-nonane ~~and β pinene~~ at 323 K. Weighted linear regression analysis for the data yields a slope with equation y = 1.00 (± 0.02) x + 0.96 (± 0.5) and an R^2 of 0.98.

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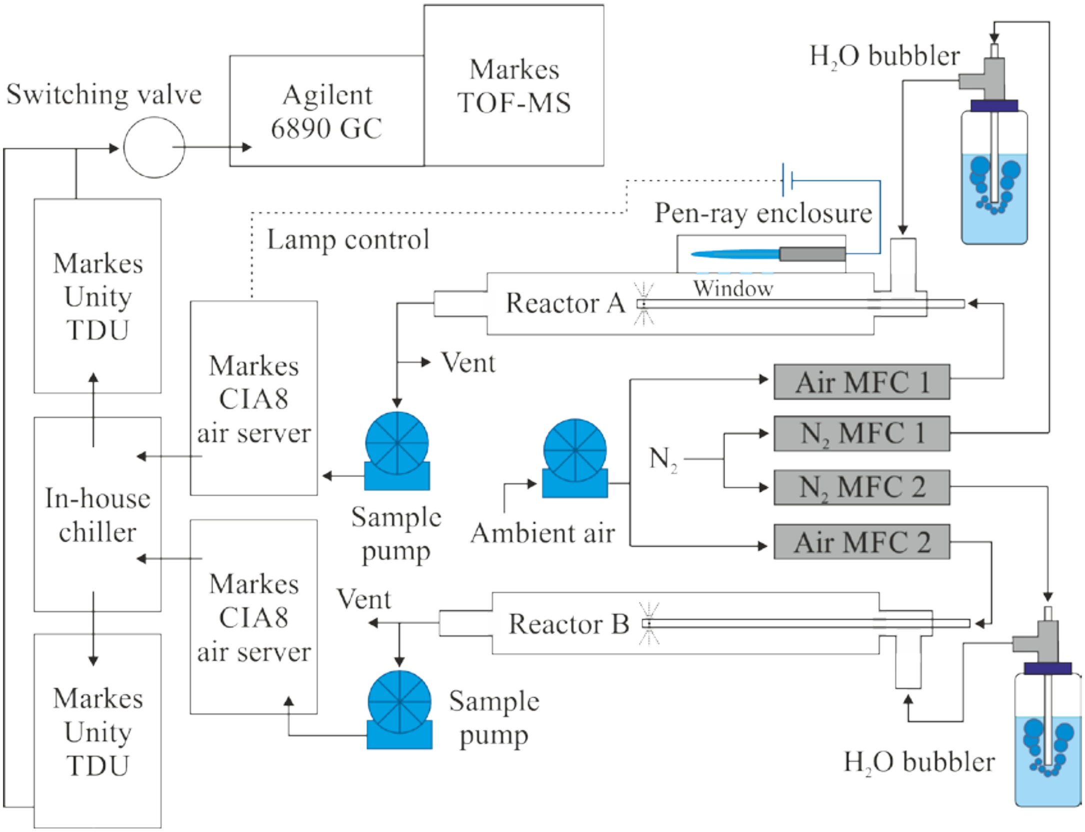

Figure 9 Schematic of the OH reactor configuration used for sampling ambient air VOC. Key to abbreviations: CIA8 = air server and canister interface accessory; GC = gas chromatograph; MFC = mass flow controller; TOF-MS = time of flight mass spectrometer; TDU = thermal desorption unit.

5

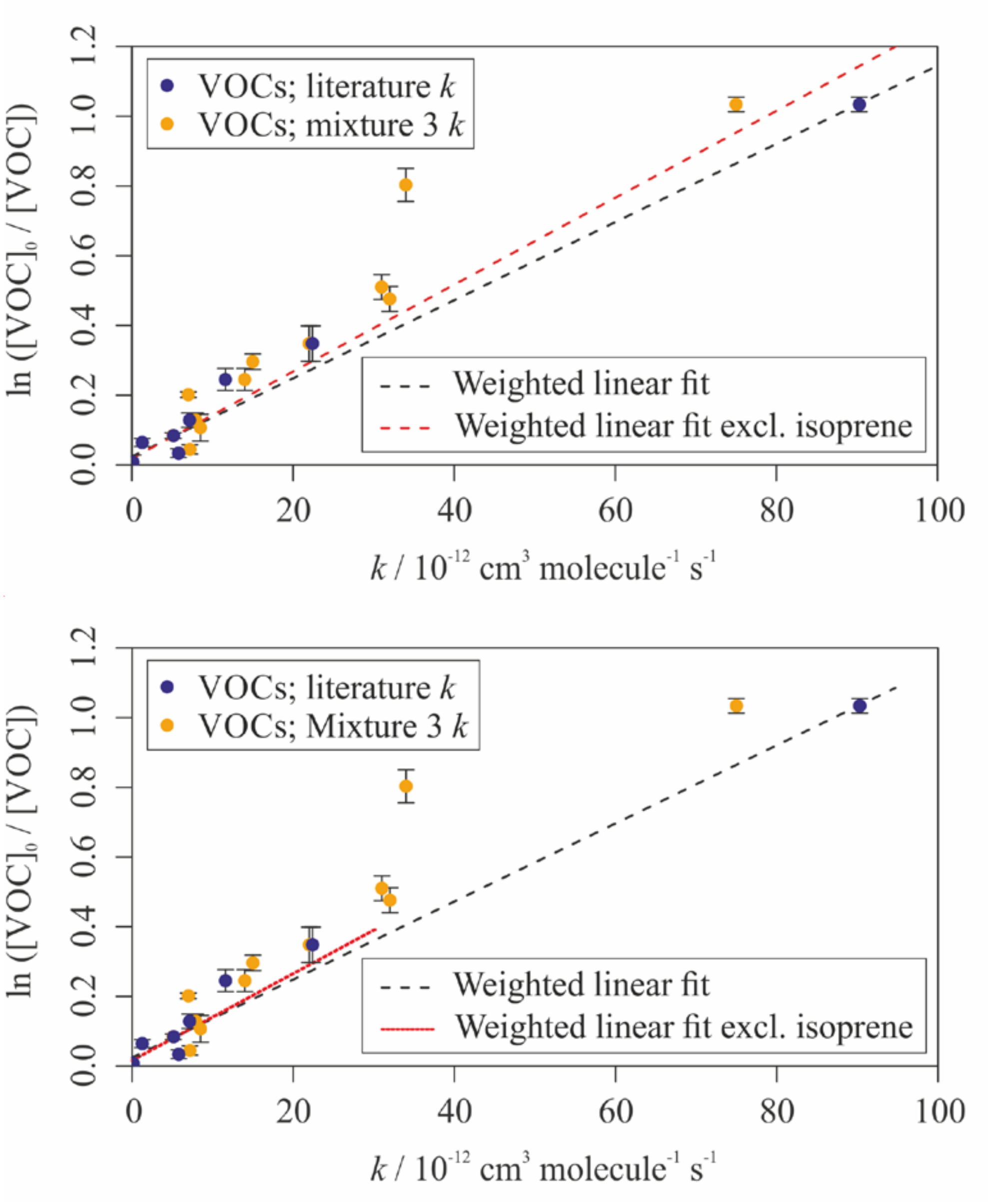

Figure 10 Relative rate plot for ambient air analysis. Compounds with a known rate coefficient are plotted using literature values at 323 K. A weighted linear fit of this data was used to generate the black dashed slope with an R^2 of 0.98. A second weighted

linear fit, excluding isoprene, is shown by the red dashed slope (R^2 of 0.71). Some of the compounds do not have literature rate coefficients at 323 K but were measured at this temperature elsewhere in this paper (see Table 3). Compounds with a rate coefficient derived from Mixture 3 relative rate studies are also plotted (in yellow) to compare between the synthetic mixture and ambient air results. Error bars on the y-axis, equal to two standard errors, are calculated using the standard deviation in ~~depletions~~depletion factors for each VOC across all samples. Error bars on the x-axis are not shown but are typically large (up to 35%).