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Interactive comment on "A self-consistent, multi-variate method for the determination of gas phase rate coefficients, applied to reactions of atmospheric VOCs and the hydroxyl radical" *by* Jacob T. Shaw et al.

Anonymous Referee #2

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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. 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.

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.

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

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

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

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

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.

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.

P5L23 “depletion” Perhaps fractional loss of a VOC ?

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.

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.

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.

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).

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

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 ?

P9L15 Replace “needs to only be a. . .” with “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.

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 ?

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.

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) ?

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).

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.

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.

P10L8 Replace “measurements” with “rate coefficient measurements”

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

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

P10L16 Replace “value” with “rate coefficient”

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.

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.

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 ?

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 non-linearity in these plots requires more rigorous examination.

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

P11L19 report the gradient along with its standard deviation.

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.

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 ?

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.

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”.

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 ?

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. 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.

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.

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

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