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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 #3

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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.

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. 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.

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

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.

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

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

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).

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

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.

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

Fig 6 Noshino should be Nishino

McGillen (2008) is missing from ref list

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