

Interactive comment on “Atmospheric degradation of 3-methylfuran: kinetic and products study” by A. Tapia et al.

A. Tapia et al.

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Items that need to be addressed:

-My main point is that the paper is too long compared to the hard facts that are presented. The authors should try to shorten it considerably e.g. by deleting words and phrases that carry little or no information and by avoiding repetition of facts,.

The authors have considered this recommendation. The sections 3.2.2, 3.2.3 and 4 have been reorganized. See the new version of manuscript.

-Rate coefficients were determined by relative methods. Perhaps a few words about error propagation in a self-consistent set of rate coefficients would be appropriate.

C11450

This paragraph has been included in the text:

In agreement with these equations, the data yield straight lines that pass through the origin with a slope of k_S/k_R indicating that secondary reactions or heterogeneous processes are insignificant. The error limit for the ratio of rate coefficients k_S/k_R includes only the precision of the fit to our experimental data ($\pm 2\%$). The k_S error limit, $\pm 10\%$, has been calculated taking into account the error limit from the slopes obtained from the regression analysis and the quoted error in the value of the rate coefficient for the reference compound.

-Are there other similar compounds with rate coefficients determined by absolute methods that could be used for comparison?

Yes there are different studies that determine the rate coefficients of similar compounds. But the aim of this study was recalculate the rate constant of 3-methylfuran in order to give a new data because previous to this work only one value of rate constant for 3-methylfuran and OH is reported in the literature (Atkinson et al. 1989) and in the case of 3-methylfuran with NO₃ the two values of rate constants reported in the literature (Kind et al. 1996, and Alvarado et al. 1996) are very different. On the other hand, there are several studies in the literature where this discussion is made (Bierbach et al. 1995, Kind et al. 1996, Cabañas et al. 2003, Cabañas et al. 2004 and Cabañas et al. 2005), so we do not consider necessary to do a comparative study of the rate constants.

-The Expression “kinetic rate coefficient” is used in several places. Remove “kinetic”
OK

-(p 1 line 6 of first version of manuscript) “absolute rate coefficients” Not obvious what is meant by “absolute”. The reaction order for which a coefficient is given is apparent from its units. Further, this number was determined by relative measurements as opposed to absolute measurements. Remove “absolute”
OK

C11451

-(p 1 lines 8-9 of first version of manuscript). The sentence “These rate coefficients...” does not carry any information. Remove OK

-(p1 line 16 first version of manuscript). “is the addition” suggest “is addition” OK

-(p 1 line 20 first version of manuscript). “for both Cl” suggest “for Cl” OK

-(p 1 line 25 of first version of manuscript) “and the degradation products of biogenics” I don’t understand – rewrite This paragraph has been rewritten. See the new version of manuscript

-(p 1 line 29-30 of first version of manuscript). If it is measured then it is detected, delete “detected”. OK

-(p 2 line 23 first version of manuscript). In principle just one rate coefficient, use singular OK

-(p 3 line 15-16 of first version of manuscript) Strictly speaking, this means that the kinetic experiments with OH were made exclusively in air and the NO₃ experiments exclusively in nitrogen. Is this true? Yes it is

-(p 3 line 17-18 of first version of manuscript). Again, strictly, “respectively” links k_s and k_r with OH and NO₃ (respectively) and I do not think this is what was meant. Rewrite this sentence. This sentence has been rewritten. See the new version of manuscript

-(p 3 line 22 of first version of manuscript). This is not the proper reference for the relative rate technique and it should be exchanged. The technique and mathematical framework was available at least as early as 1982 (e.g. Atkinson et al. Int. J. Chem. Kin.14, 781-788, 1982), possibly earlier. This reference has been included. See the new version of manuscript

-(p 5 line 7 of first version of manuscript). There is a mix of pressure units in the paper, please do not use Torr. . .

We have changed Torr for atm

C11452

-(p 5-7 of first version of manuscript). There are six? Sets of “lamps”, sometimes referred to by maker and product number, sometimes by a single wavelength. Is there a way of making this less confusing, (e. g. are the 360-lamps on p 6 l 20 the same as on p 6 l 30? The authors have considered this comment and in the new version the lamps only refer to a single wavelength. -(p 7 line14 first version of manuscript). “in” suggest “at” OK

-(p 7 line 23 first version of manuscript). suggestion remove “every” OK

-(p 8 line 25 first version of manuscript). reaction singular OK

-(p 8 line 26, first version of manuscript). were → was OK

-(p 8 lines 26-27, first version of manuscript) suggestion delete “in the experimental set-up OK

-(p 8 and elsewhere of first version of manuscript). “NO_x” the use of this concept implies that the authors do not know (but of course, they do) what they add since, by definition NO_x= NO + NO₂. Most likely they add NO that is turned into NO₂ e.g. by peroxy radicals as the reaction proceeds. It is suggested that the actual, initial gas composition is given rather than “NO_x”.

We have change NO_x for NO as the referee suggests.

-(p 11 line l 3 f first version of manuscript) change “determined” to “estimated” OK

-(p11 line 6-7 of first version of manuscript) Why should the present rate coefficient be preferred as “reference data” when it is equal within the limits of error to that proposed by Atkinson et al., and has the same error associated with it?

This means that rate coefficients obtained corroborated literature data, but not to be preferred to others. See the new version of manuscript to see the new paragraph.

-(p 11 line 21 of first version of manuscript). Are these commercial libraries or custom? They were not mentioned earlier.

C11453

The commercial libraries available with the GCMS software are NIST 21, NIST 27, NIST 107, NIST 147 and WILEY 229, Aldrich Library of FT-IR spectra Edition I V3 and a custom FTIR and GC-MS library created after the injection of commercial products. This has been included in the text.

-(p 13 line 20-21 of first version of manuscript). A reference addressing the OH-formation would be appropriate.

This reference has been included Wang et al., 2005.

-(p 14 line 17 of first version of manuscript). "the Wuppertal laboratory"???

The experiments done in order to measure the absorption coefficient for the structurally related compound 2(5H)-furanone were carried out by FTIR in the 1080 L chamber which is in the Wuppertal laboratory (physical chemistry department in the University of Wuppertal). In the text, "Wuppertal laboratory" has been changed by "using the 1080 L chamber".

-(p 15 line 4 of first version of manuscript). Why would FTIR measurements overestimate concentrations? In Villanueva et al., 2009 the reaction of 2-methylfuran and 2-ethylfuran with Cl atoms are studied. In these reaction CH₃ and CH₂CH₃ groups were ejected from the ring of 2-methylfuran and 2-ethylfuran, respectively, to form the chlorinated furanones. Then, the yield of HCHO and CH₃CHO formed from these radicals gave us the yields of the chlorinated furanones that were less than the yields estimated using the Beer-Lambert law. For this reason in the manuscript it is mentioned that the concentrations could be overestimated. In the reaction of 3-methylfuran with Cl atoms any radical is ejected from the ring because the chlorinated methylfuranone is formed with the 5 carbons, then there is not a co-product to compare the yields as in the cases of 2-methylfuran and 2-ethylfuran. In the text the reference (Villanueva et al, 2007, 2009) has been changed at the last of the sentence to indicate the work where that is explained. -(p 20 line 4-5 of first version of manuscript) the mixing ratio is less interesting than the yield – delete ppb, keep yield OK -(p 25 line 26 of first version

C11454

of manuscript). Something happened to this reference.

It is right in the last version published in ACPD

-(p 25 line 27 of first version of manuscript) This is not the proper name of the book.

The reference has been changed. Finlayson-Pitts, B. J. and Pitts, J. N.: Chemistry of the upper and lower atmosphere: Theory, Experiments and Applications. San Diego, Academic Press, 2000.

(first version of manuscript) Table 2 is (%C) and "molar yield (%)" the same thing? If so why use different nomenclature. If not, then %C needs some explanation.

Yes, it is the same. In the case of 3-methylfuran all the products have 5 carbons, therefore %C is the same as molar yield.

(first version of manuscript). Table 3 is a "one-liner", consider putting the numbers into the text or reorganize the table.

It is right in the last version published in ACPD

(first version of manuscript). Consider putting the straight line-plots (fig 1 and 2) in the supporting material and lift supporting figure 3 into the paper. Comment in the text on the intercepts in fig 1 and 2. Do they differ significantly from zero?

The authors have considered this comment and the figures have been reorganized. They do not differ significantly from zero. A paragraph has been included in the new version.

(first version of manuscript). Figure 3 has A, B, C in the wrong order. It is right in the last version published in ACPD

-(p 37 , first version of manuscript). Text to figure 4. is the timing really done with "fraction of second" resolution? Cosmetics (some points but there may be more)

It is right in the last version published in ACPD

C11455

Please also note the supplement to this comment:
<http://www.atmos-chem-phys-discuss.net/10/C11450/2010/acpd-10-C11450-2010-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 22905, 2010.

C11456