

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

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I entirely agree with referee #1 that the “substantiated results content” of the paper does not justify the length of the article and attempts should be made to shorten the manuscript. There is often too much unnecessary detail.

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.

-(p 1 line 6 first version of manuscript). The authors have put the relatively determined rate coefficients on an absolute basis using reference rate coefficients. The authors need to be care when sing “absolute” when referring to rate coefficients. OK. The word “absolute” has been deleted.

-(p 2 line 10-15 first version of manuscript). This section is a repetition of what is stated on page one, lines 27-28.

This section has been rewritten. See the new manuscript version.

-(p 5 line 7 first version of manuscript). What is a SAUTRN reaction chamber?

SATURN is the brand of Multi-Pass Gas cells of 50 L.

-(p 6 line 32 first version of manuscript). The authors appear to have performed experiments in a chamber at another institute. This chamber needs to properly referenced the first time it appears in the text.

This has been considered and changed in the manuscript

-(p 11, top section first version of manuscript). How do the rate coefficients obtained for the reactions of OH and NO₃ with 3-methylfuran compare with available literature vales for other mono- and dimethylated furans? Is any trend apparent depending on the position and extent of the methylation?

As explain above to the referee 1, the aim of this study was recalculated 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 3-methylfuran with NO₃ the two values of rate constants (Kind et al. 1996, and Alvarado et al. 1996) are very different. On the other hand, there is a previous work made by our research group where this discussion is made (Cabañas et al. 2005). Therefore, we have not included a lager discussion in the kinetic section because we do not consider necessary to do a comparative study of the rate constants.

The value of the rate coefficient for a reaction will only give an indication of the major initiating step in the degradation process, product analyses are always necessary to elucidate the subsequent steps. The last paragraph in this section could be deleted since this is what one would expect anyway.

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-This paragraph has been deleted.

-(p 11, line 21 first version of manuscript). Which mass spectra and infrared spectra libraries were used? Please state.

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 top first version of manuscript). The major fate of alpha-chloro alkoxy radicals is expected to be reaction with O₂ (Orlando et al. Chem. Rev. 2003, 103, 4657) which in this case would form the ring-retaining halogenated products observed in the analysis.

-(p 13, second paragraph first version of manuscript). I do not understand some statements made here. Concentration-time plots will always be curved (line 11). The curves can be a mixture of production and loss but it is not always easy to see this by simple inspection of the curve. If a product is secondary in nature there is usually a delay in its appearance and often there plot is curved upwards. From figure 3, for many low yield products, I personally could not say whether they are primary or secondary products.

It is true that the information given in the manuscript cannot be related to figure 3 because especially in this figure this cannot be seen easily. There are very few points due to the technique used (SPME-GC-FID) and with FTIR the most of the secondary products have not been identified due to the mixture of products that have not been subtracted due to the lack of authentic standards. We consider that these products are secondary because they can only be formed from reactions of the primary products. In addition, these secondary products are the same kind of secondary products than those obtained in the reaction of furan with Cl atoms (Villanueva et al., 2007)

-(p 14 line 22-23 first version of manuscript. why are the secondary reactions negligible in the early stages of the reaction with UV lamps? Please explain.

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At the beginning of the reaction the photolysis of the products or reaction with Cl atoms is not as evident as at the end of the reaction. This is demonstrated by the yields obtained using VIS lamps to generate Cl atoms and the yield obtained using UV lamps. These yields are only comparable in the early stage of the reaction with UV lamps, later a loss of the product is evident and the yield decay. (Bierbach et al 1995). This only could be done with FTIR where we had one spectrum every one minute. Therefore, the product yields are calculated from the slopes of plots of products formed vs. alkylfuran reacted with the mention that in an early stage of the reaction, the secondary reactions are almost negligible.

-(p 15-16 first version of manuscript). The section on the products from the reaction of OH with 3-methylfuran makes no comparison with literature product data, i. e. the studies of Bierbach et al. 1995 and Gomez Alvarez et al. 2009. These studies report high yields of the unsaturated dicarbonyls for reactions of OH with furan, 2-methylfuran and 3-methylfuran. Gomez Alvarez et al. reported yields of $\approx 83\%$ for 4-methyl-1,4-butenedial for the reaction of OH with 3-methylfuran. IT is difficult to reconcile the low yield obtained in the present work with those available in the literature (I suspect photolysis is the cause-see below). This needs to be discussed in detail. There is a reference to the studies on page 19 but not a real discussion.

We have reorganised the section 3.2.2 including a discussion about the different yields of 2-methylbutenedial as the referee suggest. See the new version of manuscript.

-(p 16 line 10 first version of manuscript). The presence of ROONO₂ compounds can easily be established by introducing NO into the system which will destroy the equilibrium $\text{ROO} + \text{NO}_2 \rightleftharpoons \text{ROONO}_2$, was such a test made? ROONO₂ compounds are generally not very stable anyway.

Yes, one experiment was made observing that the intensity of the bands at 1297 and 1735 cm⁻¹ decreased after the addition.

-(p 16 line 11 first version of manuscript). I do not find the assignment of the carbonyl

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absorption at 1820 cm⁻¹ to hydroxyl-methylfuranones very convincing without support from other IR absorptions such as from the OH-group. Many different types of carbonyls absorb around the 1800 cm⁻¹ region.

Analyzing the IR spectra (figure 4C) it can be seen a band at 1014 cm⁻¹ what supports the presence of a compound type hydroxyl-methylfuranone. In the new version of manuscript the text has been changed. See new version of manuscript.

-(p 16 Reaction with NO₃ radicals, first version of manuscript): this section is very speculative and is full of “could be’s” statement without any firm identification. I suggest that this section could be considerably shortened. In this section the authors suggest the presence of ROONO₂ and –C(O)O₂NO₂ groups. Here again introduction of NO could easily establish this. Was is done?

The authors consider that the results and discussion of the products are very important and all details described here are necessary in order to understand the work. In addition, although many products especially nitrated have not been confirmed due to the lack of commercially available standards these results can be used in the future to identify and to establish the real mechanism of the reaction of 3-methylfuran with NO₃ radicals. This section has been rewritten. We can assure that the assignment of the IR bands has been meticulous based on bibliographic references, comparing with the IR spectra of similar compounds and with our previous works such as the reactions of furan and alkylfurans with Cl atoms and although there are many “could be” all the reasoning are logical, therefore we consider that cannot be deleted from the text.

The presence of ROONO₂ is supported by the fact that the absorption bands corresponding to 792, 1732 and 1294 cm⁻¹ (typical of these compounds) decrease along the time. This same observation is reported by Hjorth et al., 1990; Wängberg and Ljungström, 1992. 2) so in this case the addition of NO was not necessary.

-(p 16 line 7 first version of manuscript). The assignment of the absorption at 820 cm⁻¹ to an epoxy compound is very speculative based on just the one absorption.

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Depending on the type of epoxide strong bands should also occur at other frequencies. In the type of epoxide which would be formed in the present study there should an equally strong and sharp absorption due to a C-H vibration at around 3000 cm^{-1} . Was this the case? If so would have a little more faith in the assignment.

In our experiments the band at 820 cm^{-1} (intense) together with the band at 1021 cm^{-1} could correspond to an epoxy compound. This same assignation was done by Martin, P. et al. in the study of 4,5-dihydromethylfuran with NO_3 . The band at 3000 cm^{-1} is observed in the spectrum but it is typical of C-H vibration and it can come from any other compound with C-H bonds in its structure such as nitrooxy-methylfuranone, nitroperoxy-furanones, etc. See scheme 5.

-(p 19 line 18 first version of manuscript). The low yields of 2-methylbutenedial in the system are more likely to be due to photolysis of the compound rather than reaction with OH. 2-methylbutenedial has a very fast photochemistry. Even though the authors did not quantify 2-methylbutenedial in the IR spectrum they be able to estimate the lifetime of 2-methylbutenedial in the reaction system from the absorption-time behavior of the IR bands.

As the referee suggests, the analysis of the IR band at 1711 cm^{-1} typical of 1,4-dicarbonyl compounds has been done. Figure 1 shows the plot of the absorbance intensity versus time, the curved shape indicates that from ≈ 23 min the 2-methylbutenedial concentration decreases due to secondary reactions. Plotting $\ln(A_0/A_t)$ versus time from 23 min, data show a photolysis rate of 0.0261 s^{-1} , see figure 2.

-(p 20 and other sections of the text first version of manuscript). There is enough kinetic data available on C-H abstraction reactions with OH, Cl and NO_3 to estimate just how much of the reactions will be proceeding by H-atom abstraction. How important is the abstraction route really based on available SAR and kinetic data? Limits could definitely be set on the extent of this channel.

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In order to know how important the H-atom abstraction route is from the methyl group for the reaction of 3-methylfuran with Cl, OH and NO₃, SAR method has been used to estimate the 3-furaldehyde molar yield. Therefore, we can check if the yields of 3-furaldehyde measured with Cl, OH and NO₃ are consistent with what one would expect from SARs using the ratio $k(\text{H-atom abstraction from CH}_3)/k(\text{overall rate coefficient for Cl/OH/NO}_3 + \text{3-methylfuran})$. This ratio has been calculated firstly using the half of the rate constant of ethane and the rate constant of 3-methylfuran with every oxidant, table 1, and secondly using the H-abstraction rate constant of –CH₃ group calculated by SAR method and the rate constant of 3-methylfuran, table 2. The molar yields calculated and determined experimentally are shown in table 3.

Molar yields data calculated and determined experimentally for the reaction of 3-methylfuran with Cl agree into experimental error. However molar yields in the case of 3-methylfuran reaction with OH and NO₃ do not agree. Therefore in these cases the SAR method is not consistent with the experimental results. We cannot explain this discrepancy, in our experiments the yield of 3-furaldehyde is well established in especial for the reaction of 3-methylfuran with OH radical where the quantification was made using two different techniques, GC-MS and GC-FID obtaining similar yields (2.83 ± 0.63 and 3.95 ± 1.85) into the experimental errors.

-(p 21 line 21 first version of manuscript). Based on the evidence presented I find this very speculative especially in light of the results from other product studies on OH with furan, 2-methylfuran etc.

In the last version published in ACPD we comment that this assumption is made on the basis that the mechanism to form 5-nitrooxy-2(5H)-methylfuranones is the same as that proposed for the formation of 5-chloromethyl-2(5H)-furanones whose yields are >16 and > 25 using SPME-GC-FID.

-(p 36 Figure 3 first version of manuscript). It would be better if the running order was from top to bottom A, B, C as in Figure 4. It is right in the last version published in ACPD

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/10/C11457/2010/acpd-10-C11457-2010-supplement.pdf>

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

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2010

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Table 1. Rate constants for the reaction of ethane with Cl, OH and NO₃ at room temperature.

Reaction	k/ cm ³ molec. ⁻¹ s ⁻¹	Bibliographic reference
Ethane + Cl	5.9x10 ⁻¹¹	Atkinson et al., 1997
Ethane + OH	2.55x10 ⁻¹³	Atkinson et al., 1997
Ethane + NO ₃	1x10 ⁻¹⁷	Atkinson et al., 1997

Table 2. Rate constants and substituent factors for the H-atom abstraction reaction of –CH₃ with Cl, OH and NO₃.

	k _{prim}	F(>C<)	k (CH ₃) / cm ³ molec. ⁻¹ s ⁻¹	Bibliographic reference
Cl	3.32·10 ⁻¹¹	0.79	2.62·10 ⁻¹¹	Aschmann and Atkinson, 1995
OH	0.144·10 ⁻¹²	1.29	1.86·10 ⁻¹³	Atkinson, 1985
NO ₃	-	-	-	-

$$k(\text{CH}_3) = k_{\text{prim}} \times F(>\text{C}<)$$

Table 3. Molar yield of 3-furaldehyde in the reaction of 3-methylfuran with Cl, OH and NO₃ estimated from SAR method.

Reaction	k/ 10 ¹⁰ cm ³ molec. ⁻¹ s ⁻¹	(k _{ethane} /2)/k _{3-methylfuran}	k(CH ₃)/k _{3-methylfuran}	3-Furaldehyde molar yield ^a / %
3-Methylfuran + Cl	4.20	0.070	0.062	7.0-9.0
3-Methylfuran + OH	1.1 ^b	0.001	0.002	3.95
3-Methylfuran + NO ₃	0.13 ^b	3.85·10 ⁻⁷	-	0.36

^a Cabanas et al., 2005. ^b This work.

Molar yields data calculated and determined experimentally for the reaction of 3-methylfuran with Cl agree into experimental error. However molar yields in the case of 3-methylfuran reaction with OH and NO₃ do not agree. Therefore in these cases the SAR method is not consistent with the experimental results.

We cannot explain this discrepancy, in our experiments the yield of 3-furaldehyde is well established in especial for the reaction of 3-methylfuran with OH radical where the quantification was made using two different techniques, GC-MS and GC-FID obtaining similar yields (2.83±0.63 and 3.95±1.85) into the experimental errors.

References

- Atkinson, R.: Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds under Atmospheric Conditions. Chem. Rev., 1985, 85, 69-209.
- Aschmann, S. M. and Atkinson, R.: Rate constants for the gas phase reactions of alkanes with Cl atoms at 296±2 K. Int. J. Chem. Kinet., 27, 613-622, 1995.
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Fig. 1.

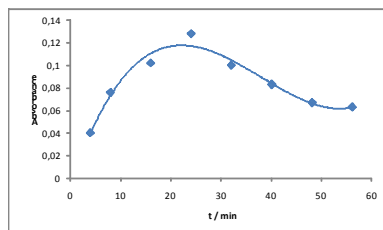


Figure 1. Plot of the absorbance intensity of the band at 1711 cm^{-1} versus time.

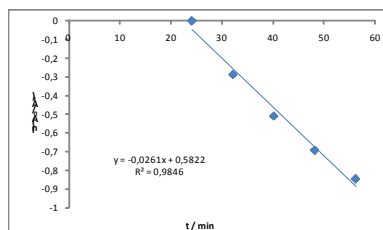


Figure 2. Plot of the $\ln(A_0/A_t)$ versus time for 1711 cm^{-1} band.

Fig. 2.

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