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

Anonymous Referee #2

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The paper describes a kinetic and product study on the reactions of OH, NO₃ and Cl with 3-methylfuran. Rate constants are reported for the reactions of OH and NO₃ with the 3-methylfuran determined with the relative kinetic method and several different analytical techniques and reference hydrocarbons. These are not the first rate constant determinations but for OH with 3-methylfuran there has been only one previous investigation and for NO₃ with 3-methylfuran there is a factor of 2 discrepancy between the two available investigations.

Detailed product analyses on the reactions of OH, NO₃ and Cl with 3-methylfuran have been performed using SPME combined with GC/MS and GC/FID and in situ FTIR as analytical techniques, whereby only the OH reaction has been studied previously. Using the product information obtained from analyses reaction mechanisms are postu-

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lated for the reactions of OH, NO₃ and Cl with 3-methylfuran.

There is enough material to justify publication; however, I have the following remarks on the paper that need attention before publication. The anonymous referee #1 has already made a lot of comments on the text and content, most of which I agree with, and I will therefore restrict most of my comments to other matters.

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. At Page 1, line 6: the authors have put the relatively determined rate coefficients on an absolute basis using reference rate coefficients. The authors need to be care when using “absolute” when referring to rate coefficients. At Page 2, lines 10-15: this section is a repetition of what is stated on page one, lines 27-28. At Page 5, line 7: what is a SATURN reaction chamber? At Page 6, line 32: 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. At Page 11, top section: How do the rate coefficients obtained for the reactions of OH and NO₃ with 3-methylfuran compare with available literature values for other mono- and dimethylated furans? Is any trend apparent depending on the position and extent of the methylation? 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. At Page 11, line 21: which mass spectra and infrared spectra libraries were used? Please state. At Page 13, top: 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. At Page 13, second paragraph: 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

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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. \rightarrow Page 14, lines 22-23: why are the secondary reactions negligible in the early stages of the reaction with UV lamps? Please explain. \rightarrow Pages 15-16: 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 $\sim 83\%$ 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 no real discussion. \rightarrow Page 16, line 10: The presence of ROONO₂ compounds can easily be established by introducing NO into the system which will destroy the equilibrium ROO + NO₂ \leftrightarrow ROONO₂. Was such a test made? ROONO₂ compounds are generally not very stable anyway. \rightarrow Page 16, line 11: I do not find the assignment of the carbonyl 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. \rightarrow Page 16, reaction with NO₃ radicals: This section is very speculative and is full of “could be’s” statements without any firm identification. I suggest that this section could be considerably shortened. In this section the authors suggest the presence of ROONO₂ and $-\text{C}(\text{O})\text{O}_2\text{NO}_2$ groups. Here again introduction of NO could easily establish this. Was this done? \rightarrow Page 16, line 7: The assignment of the absorption at 820 cm⁻¹ to an epoxy compound is very speculative based on just the one absorption. Depending on the type of epoxide strong bands could 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 I would have a little more faith in the

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assignment. Page 19, line 18: 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. Page 20 and other sections of the text: There is enough kinetic data available on C-H abstraction reactions with OH, Cl and NO₃ 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. Page 21, line 21: 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. Page 36, Figure 3: It would be better if the running order was from top to bottom A, B, C as in Figure 4.

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