

Atmos. Chem. Phys. Discuss., author comment AC1
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Reply on RC1

María Asensio et al.

Author comment on "Evaluation of the daytime tropospheric loss of 2-methylbutanal" by
María Asensio et al., Atmos. Chem. Phys. Discuss.,
<https://doi.org/10.5194/acp-2021-758-AC1>, 2021

We greatly appreciate the Referee #1's comments on our work that certainly help us to improve the quality of the submitted manuscript. In the following sentences we reply to the comments.

Reply to Specific Comments:

- *In the abstract, the authors have a typo on the rate coefficient for Cl atoms reaction with 2MB. The correct order should be 10^{-10} , i.e., $k(298\text{ K}, 760\text{ Torr}) = (2.16 \pm 0.16) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.*

Authors' reply: Yes, it was a typo. We will correct it in the revised version of the manuscript that will be uploaded after the discussion is finished.

- *Although tropospheric chemistry (OH and Cl) and photolysis are expected to dominate the atmospheric degradation of 2MB, deposition should not be neglected, especially in the case that a unique product might be formed during wet or dry deposition followed by on surface hydrolysis. It might be worth the authors to address that in the introduction.*

Authors' reply: As far as we know, there is a lack of information on the dry and wet deposition of 2-methylbutanal. However, following the Reviewer's advice, we have included a sentence in the introduction to point out the possibility of deposition as a sink for this compound, similarly to acetaldehyde, for which deposition is a minor sink (Millet et al.; Atmos. Chem. Phys., 10, 3405–3425, 2010). In fact, it is possible to estimate the lifetime of 2MB when only wet deposition is considered (t_{Wet}) since its Henry's Law constant is known ($k_{\text{H,cp}} = 2.33 \text{ M atm}^{-1}$ (Pollien et al.; Int. J. Mass Spectrom., 228, 69-80, 2003)). t_{Wet} can be estimated from the following equation (Chen et al.; Atmos. Environ., 37, 4817–4822, 2003):

$$t_{\text{Wet}} = \frac{z}{v_p R T k_{\text{H,cp}}}$$

where z is the altitude, v_p is the precipitation rate, that can be considered as 0.43 m

year^{□1}, which is the annual average precipitation in Valencia (Spain), R is the gas constant and T is temperature, that can be considered to be 298 K. Taking all this into account, and considering different altitudes between 100 and 2000 m, t_{Wet} is estimated to range between 4 and 82 years, depending on the considered altitude. If this estimation is compared with the tropospheric sinks discussed in the original manuscript, it is clear that wet deposition is a negligible sink for this compound.

- *The authors should give in the text the magnitude of the total corrections (in the whole course of the measurement, e.g., total reaction or photolysis time) has been made, in kinetic and photolysis measurements, due to other than the primary processes of interest. This way the reader can evaluate the accuracy of the measurements and the potent errors that these corrections introduce.*

Authors' reply: The correction made in the Cl-reaction kinetic experiments, as described in the manuscript, includes the overall losses for both 2MB and the reference compound (heterogeneous reaction onto the reactor walls, UV photolysis and/or reaction with the oxidant precursor). If this correction had not been applied, the rate coefficient would have been $(2.07 \pm 0.31) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which shows a 4% difference with the corrected result: $(2.16 \pm 0.32) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The contribution of the mentioned losses will be included in the revised manuscript.

For the photolysis experiments, only the loss onto the walls of 2MB was considered. If no correction had been done, the result would have been $(2.57 \pm 0.15) \times 10^{-5} \text{ s}^{-1}$ instead of $(1.96 \pm 0.32) \times 10^{-5} \text{ s}^{-1}$, so they are 24% different. The magnitude of this correction was already mentioned in Section 2.1.2, and in the revised version that will be pointed out when presenting the results.

- *As expected, OH chemistry dominates the lifetime of 2MB and thus it would have been of interest to determine OH + 2MB reaction products in a chamber experiment, since PLP-LIF method would not allow that. Were there any limitations that did not allowed the authors to look into OH initiated chemistry end-products determinations?*

Authors' reply: As pointed out by the Reviewer, the PLP-LIF experimental set-up used in the kinetic study of the OH-reaction does not allow to determine end-products of the reaction and a chamber experiment would be useful. However, to detect reaction products from OH+2MB reaction in our chambers some experimental complications arise. The chamber coupled to the FTIR spectrometer is made of Pyrex, not quartz, which forces us to use actinic lamps ($\lambda_{\text{max}} = 360 \text{ nm}$). At this wavelength, $\text{CH}_3\text{ONO}/\text{O}_2/\text{NO}$ should have been used as the OH-precursor. As NO is needed to convert HO_2 radical into OH, its presence would change the fate of the radicals formed in the OH+2MB reaction and different reaction products than those formed in the absence of NO would be formed, making harder to interpret the FTIR spectra because of the overlap of the IR bands. To get cleaner reaction mixture, photolysis of H_2O_2 by germicide lamps ($\lambda_{\text{max}} = 254 \text{ nm}$) should be used to generate OH radicals. These lamps can only be used with the 264-L chamber, that has quartz windows, but photolysis of both 2MB and reaction products can also occur complicating the FTIR spectrum after irradiation with new bands from photolysis products or increasing the intensity of the IR bands that are common to reactive and photolysis processes. Monitoring the Cl-reaction products is usually easier than for the OH-reactions since the actinic lamps ($\lambda_{\text{max}} = 360 \text{ nm}$), used to photolyze Cl_2 , minimize the photolysis of 2MB and reaction products. As measured in this work, the absorption cross section of 2MB at 360 nm is much lower, $(0.03 \pm 0.08) \times 10^{-20} \text{ cm}^2$, than that at 254 nm, $(1.01 \pm 0.09) \times 10^{-20} \text{ cm}^2$. Moreover, Cl atoms are less selective than OH radicals, so the Cl-reaction usually yields the same products than OH-reaction and some other products too. Then, we decided that the information obtained in the study of the products of the Cl-reaction

should be enough to understand the atmospheric implications of 2-methylbutanal. In fact, there are previous works that look at the Cl-reaction products to understand the products of the OH-reaction, such as the study of the unsaturated aldehydes published by Orlando and Tyndall (*J. Phys. Chem. A* **2002**, *106*, 12252-12259).

- *Although the authors clearly report how they have estimated 2MB lifetime at Valencia atmosphere, the use of a peak Cl-concentration and treating that as a constant diurnally is deceptive, particularly since after dawn, Cl concentration is expected to be rapidly decreased. The constant [Cl] treatment leads to an unexpectedly high impact of Cl chemistry on 2MB loss especially after 18:00. It might be worth the authors to revisit their analysis and try to address that.*

Authors' reply: We agree with the Reviewer that the effect of Cl atoms on the total loss of 2MB is overestimated in our work since we considered a constant peak concentration, $[Cl]_{peak}$ of 10^5 cm^{-3} . For the first hours of the day, $[Cl]_{peak}$ could probably work fine, but the Referee is right when pointing out that the impact is surprisingly (and erroneously) high after 18:00. As far as we know, there is no hourly measurements of [Cl] in Valencia (Spain) or a similar location. That makes hard to provide an accurate hourly contribution of Cl atoms to the loss of 2MB. From 20:00 h, obviously solar radiation, that can generate both Cl atoms and OH radicals, is less intense. Therefore, we will remove the relative contributions of OH, Cl, photolysis at 20:00 and 22:00 in Figure 9. Anyways, we will keep them for the rest of the day, taking into account that, even using $[Cl]_{peak}$, the major tropospheric route for the homogeneous loss of 2MB is the OH-reaction. Figure 9 will be replaced by this one:

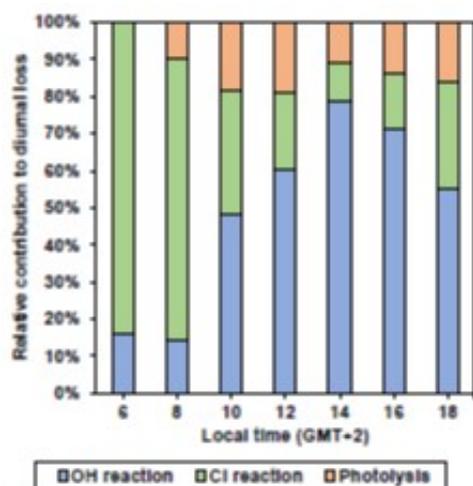


Figure 9. Relative contribution of the three removal routes studied in this work to the total diurnal loss.

Following the Referee 2's suggestion, we will also include in the revised manuscript the estimation of the tropospheric lifetime considering the average concentrations in 24 h of OH and Cl, and averaged values of the solar spectral actinic flux for 24 h in Valencia. The following text will be included:

"Considering 24 h-average values of [OH] ($1 \times 10^6 \text{ radicals cm}^{-3}$, Krol et al., (1998)), [Cl] ($1 \times 10^3 \text{ atoms cm}^{-3}$, Singh et al. (1996)), and $F(\lambda, z, q)$ for Valencia in June, t can be estimated as 7.5 h for a 24 h-period, with a relative contribution of 73% of the OH-reaction, 27% of photolysis, and less than 1% of the Cl-reaction."

- *A conclusion section in which the conclusive findings of this work would be summarized is entirely missing from the manuscript and could be extremely helpful for the communication between the authors and the reader to evaluate this nice piece of work, particularly since there is quite extensive information. It is strongly recommended to be added.*

Authors' reply: We really thank the Reviewer for this comment. Although some conclusions were included at the end of the "Atmospheric Implications" section, we will certainly add a "Conclusions" section in the revised version of the manuscript to summarize the findings of this work:

5. Conclusions

This work presents the relative importance of the most important diurnal atmospheric degradation routes of 2MB and the formation of secondary pollutants (particulate matter and gaseous products). In particular, it presents the study of the UV photolysis kinetics at (298 ± 2) K and (760 ± 3) Torr; it describes, for the first time, the temperature dependence of the OH reaction between 263 and 353 K and at P = 50–600 Torr of He, and it reports, for the first time, the rate coefficient of the Cl reaction at 298 K and 760 Torr. It was found that OH-reaction is the main removal route for 2MB at central times of the day, with a relative contribution of 79% at 14:00 LT on a day of June in Valencia (Spain) and a tropospheric lifetime of 1 h. In terms of the degradation products, butanone, acetaldehyde, or methylglyoxal were detected as major products in the Cl-reaction, together with CO and HCl. During photolysis, butane, butanone, and CO were among the products identified. SOA formation was detected, although at yields lower than 0.70%. The carbonyl products formed can contribute to photochemical smog, impacting on human health, whereas HCl can contribute to acid rain, the real impact will depend on the amounts of 2MB emitted to the troposphere.

Reply to Technical Corrections

All small changes suggested by the Reviewer will be addressed in the revised version of the manuscript and not listed here.

- *Pg 3. line 81: Please add reference for U.S. Standard Atmosphere.*

Authors' reply: In the revised manuscript, the reference for U.S. Standard Atmosphere will be included:

Gueymard, C. A., Myers, D., and Emery, K.: Proposed reference irradiance spectra for solar energy systems testing, *Solar Energy*, 73, 443-467, [https://doi.org/10.1016/S0038-092X\(03\)00005-7](https://doi.org/10.1016/S0038-092X(03)00005-7), 2002.

- *Pg 7. line 187: The phrase "with an air flow by means a dynamic inlet..." is not clear to the present reviewer. Please revise.*

Authors' reply: There was a typo in this sentence. In the revised manuscript it will state: "with an air flow by means of a dynamic inlet dilution system".

The "dynamic inlet dilution system" is an add-on of the PTR-ToF-MS instrument that is used to dilute the sample gas flow by a clean gas flow to lower the sample gas concentration in a defined way. This is necessary when the concentration of a sample compound exceeds several ppm, which negatively affects the quantification. The sample gas flow is diluted by adding a defined clean gas flow, mixing with the sample, and then subtracting a different defined flow from the mixture, so a lower flow is introduced in the reaction chamber. This approach has the advantage that the sample gas does not need to pass through any components, such as flow controllers, which could impact the trace concentrations through surface interactions, etc.

- Pg 10. lines 249 – 251: Please rephrase the whole sentence to avoid confusion.

Authors' reply: The sentence will be rephrased as: "In addition, Y_{CO} was observed to increase when the initial concentration of 2MB decreased. On the other hand, butane was quantified...".

- Pg 11. line 269: "Therefore, ...products" is a very generic statement. It is suggested to just say that have not been assigned to other atmospheric oxidation products.

Authors' reply: The sentence will be rephrased in the revised manuscript as: "However, the remaining IR bands in the residual spectrum could not be assigned to other gaseous oxidation products."

- Pg 12. line 274-275: Please rephrase to avoid confusion.

Authors' reply: The sentence will be rephrased in the revised manuscript as: "For that reason, after 150 min of photolysis, the maximum photolysis time used in this work, the content of the photolysis cell was transferred to the 16-L chamber and diluted in synthetic air. This diluted sample was flowed through the PTR-ToF-MS during 5 min, in which mass spectra were measured. From the averaged mass spectrum, the products formed after 150 min of irradiation were identified. Therefore, no temporal evolution of products was measured."

- Pg 12. line 285: Please replace " $k_{OH}(T=263-353\text{ K})$ " with " $k_{OH}(T)$ ".

Authors' reply: We decided to add the temperature range to emphasize that the shown expression is valid only in that range. We believe that it is better to show it in this way to make it clear to the reader; however, we will replace $k_{OH}(T=263-353\text{ K})$ by $k_{OH}(263-353\text{ K})$ for simplicity.

- Pg 15. Table 4: The quoted error limit in the average does not seem correct or the result from error propagation. If you include the extremes of the k measured based on the two reference reactions, k with error limits should be: $(2.16 \pm 0.32) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in the case you don't want to use asymmetric error limits.

Authors' reply: We thank the Referee for pointing out that the error limits in Table 4 were not correct. We stated in the beginning of the manuscript that errors were quoted as $\pm 2s$, but the table contained them as $\pm s$. We will correct Table 4 in the revised manuscript so the errors in k_{Cl} are $\pm 2s$:

Table 4. Results obtained in the kinetic experiments for the gas-phase reaction of Cl with 2-methylbutanal at $298 \pm 2\text{ K}$ and $760 \pm 5\text{ Torr}$ of air.

Reference	k_{Cl}/s	$k_{Cl}/10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$k_{Cl}/10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
Ethanol	2.140 ± 0.038	$1.00 \pm 0.06^{\dagger}$	2.14 ± 0.27
Isoprene	0.509 ± 0.003	$4.30 \pm 0.58^{\ddagger}$	2.19 ± 0.59
Average			2.16 ± 0.32

[†] Adkinson et al. (2006), [‡] Orlando et al. (2003)

- Pg 16. lines 334-336: It should have been possible to discriminate formaldehyde from acetaldehyde pretty easily. The features are rather discrete and IR spectra readily available. Please elucidate.

Authors' reply: We agree with the Referee. The IR spectrum of $HC(O)H$ and $CH_3C(O)H$ can be easily differentiated; however, at the very low absorptions observed in the residual spectrum, the quantification of these compounds by spectral subtraction was neither accurate nor reproducible. In addition, given that formaldehyde and acetaldehyde share

the position of some bands (for example, the C=O stretching at 1750 cm^{-1}) and other products such as propanal and 2-butanol can also interfere at some other bands, we decided not to present these inaccurate results in the manuscript. In the revised version of the manuscript, the problems found in the quantification of HC(O)H and CH₃C(O)H will be pointed out.

- *Pg 18-19. lines 378-381: Rephrase to avoid confusion.*

Authors' reply: The sentence will be modified in the revised manuscript as: " Y_{SOA} was observed to increase as the maximum value of M_{SOA} detected in the experiment increased. In previous works (Antiñolo et al., 2019; Antiñolo et al., 2020), this trend was described by the gas/particle absorption model proposed by Pankow (1994a, b) and fitted to the equation proposed by Odum et al. (1996)."

- *Graphs: In all graphs it would be easier for the reader to see the units in parenthesis without math signs, e. g., instead of Wavenumber / cm^{-1} , use Wavenumber (cm^{-1}).*

Authors' reply: We agree with the Reviewer that it can be easier for readers if units are in brackets, for example, in a graph like the shown in Figure 5 in which it is hard to say what the magnitude is and what the units are, but IUPAC recommends to note the units as we presented them in our tables and graphs (see the manual *Quantities, Units and Symbols in Physical Chemistry*) and we believe that we should follow the IUPAC recommendation.

Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2021-758/acp-2021-758-AC1-supplement.pdf>