

REVIEW BY EDITOR

We kindly thank the editor for considering this manuscript for publication and for the following comments that will help us to improve the quality of the paper.

1) Line 365, and Figure S9/Table S4: It doesn't appear to me that any correction has been made to the product concentrations for their loss due to reaction with Cl-atoms. Please apply these corrections to give the 'corrected' yield data.

Authors' reply: The editor is right: the reported yields in the original manuscript were not corrected to account for the product loss due to Cl reaction. The concentration of the products can be corrected by means of a factor given by equation (1) as in previous works (e.g., Ceacero-Vega et al. J. Phys. Chem. A, 116, 4097–4107, 2012):

$$F = \frac{k_{2MB} - k_{prod}}{k_{2MB}} \times \frac{1 - \frac{[2MB]_t}{[2MB]_0}}{\left(\frac{[2MB]_t}{[2MB]_0}\right)^{k_{prod}/k_{2MB}} - \frac{[2MB]_t}{[2MB]_0}} \quad (1)$$

where k_{2MB} is the rate coefficient for the 2MB + Cl reaction determined in this work and k_{prod} is the rate coefficient of the Cl-reaction of the product: $k_{butanone} = 4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC recommendation), $k_{acetaldehyde} = 8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC recommendation), and $k_{methylglyoxal} = 4.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Green et al., Int. J. Chem. Kinet., 22, 689-699, 1990). The corrected product yields can be determined from the slope of the plot of the product concentration corrected with the F factor *versus* $\Delta[2MB]$. Figures A and B show the non-corrected and corrected product yield plots for the FTIR and PTR-ToF-MS techniques, and Table A summarizes the results obtained without and with correction. In the revised manuscript, the reported product yields in Table S4 and Figure S9 are those corrected with F factor.

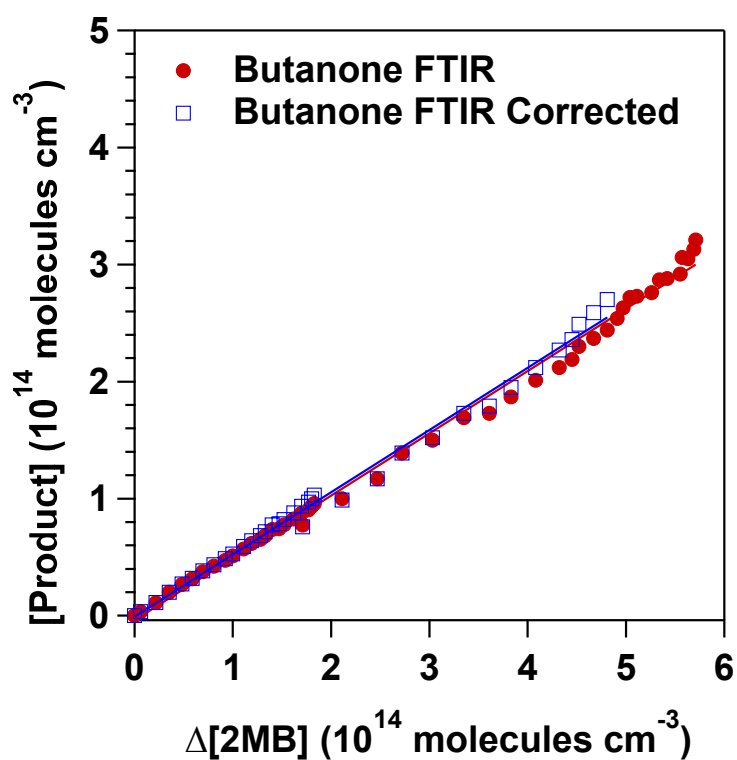


Figure A. Comparison between the non-corrected and corrected product yield for butanone quantified by FTIR.

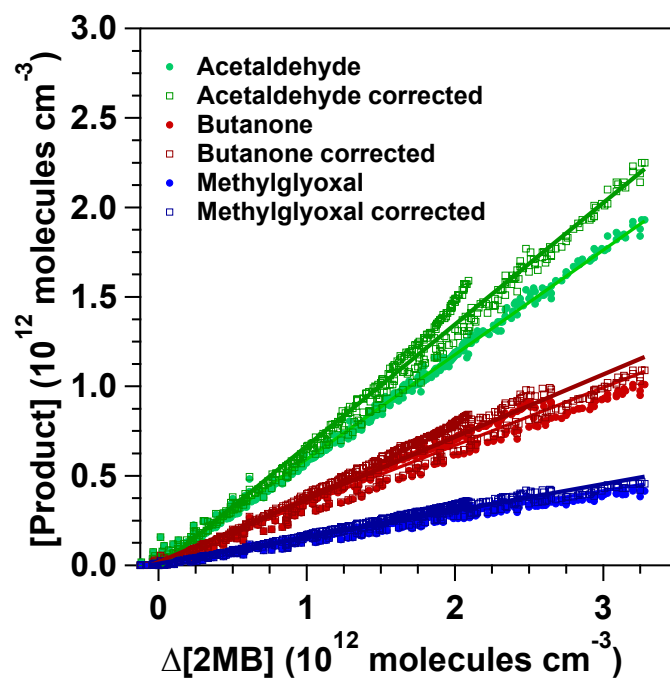


Figure B. Comparison of the non-corrected and corrected product yields for acetaldehyde, butanone, and methylglyoxal quantified by PTR-ToF-MS.

Table A. Summary of the product yields.

Compound	Detection method	Non-corrected Yield (%)	Corrected Yield (%)
Butanone	FTIR	49.3 ± 0.8	53.1 ± 1.6
	PTR-ToF-MS	32.4 ± 0.2	34.9 ± 0.6
Acetaldehyde	FTIR	-	-
	PTR-ToF-MS	58.4 ± 0.2	67.9 ± 0.8
Methylglyoxal	FTIR	-	-
	PTR-ToF-MS	13.5 ± 0.2	14.8 ± 0.2

As can be seen both in Figs A and B, and in Table A, the differences between the corrected and non-corrected yields are quite small, between 1 and 10%, and that is the reason why the correction was not applied in the submitted manuscript. Since the editor thinks that the correction should be included, we have modified Fig. S9 and Table S4 to account for this correction, and a sentence is included in the manuscript to indicate that a correction was done.

2) Near Line 411: *I agree that the reaction at the 1- and 2-position likely are most important but I am not sure that there is sufficient evidence here to confirm that, as methylglyoxal may not be a major product of reaction at the CH₂ group? Perhaps some re-phrasing of the sentence beginning on Line 411 would be helpful?*

Authors' reply: The sentence the editor referred to has been rephrased as follows in the revised manuscript:

The product yields obtained in this work indicate that the channels for the H-abstraction from the -C(O)H group and the tertiary H in C-2 are more favoured, given that Y_{butanone} is more than 2 times higher than $Y_{\text{methylglyoxal}}$. *In addition, methylglyoxal may not be a major reaction product from H-abstraction from the C-3 site.*

3) *In the mechanism, the CH₃CH₂O radical will react with O₂ to make CH₃CHO, not decompose - please change this throughout.*

Authors' reply: The decomposition of the CH₃CH₂O radical has been changed throughout the mechanisms (Figs. S13 and S14) by its O₂ reaction to form CH₃C(O)H and HO₂.

Lastly, I note a few places where grammatical improvements can be made. Please replace the current text with the words/phrases listed below.

Authors' reply: The small changes concerning the grammatical improvements suggested by the editor have been considered in the new revision of the manuscript.

REPLY TO REFEREE #1

We thank the Referee for the comments and suggestions made to improve the manuscript.

The only remaining issue is related to tables and graphs units presentation. A minor comment that also noted previously, 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). However, this is a minor technical change and does not affect the high quality of the paper.

Authors' reply: As the reviewer said, the suggested change is indeed a minor technical issue. Even though the IUPAC recommends the use of “/” to separate the magnitude and its units in tables and the legend of graphs, we have replaced “/” by “()” for ease of reading in all tables and figures of the revised manuscript and supporting information.

REPLY TO REFEREE #2

We really appreciate the Referee's comments and have tried to address them successfully.

Cross-sections for product quantification: To extend the impact of these observations, it would be useful to include the absolute IR cross-sections used to quantify the 2-MB and the oxidation products in this work. This could be done in a number of ways. For example, the Y-axes of Figure S6 could be shown in cross-section units, or a Table of integrated band cross-sections could be included, or single point cross-sections could be given for strong lines (with instrumental optical parameters).

Authors' reply: In the present work, the absolute IR absorption cross sections at each wavenumber were determined from the slope of the Beer-Lambert's plot. As this information can be useful for other researchers to quantify 2MB, we have included an Excel file with all σ_v in the supporting information. If needed by other researchers, they can easily use the tabulated IR absorption cross sections to obtain the integrated cross sections in the desired wavenumber range, or even to extract the single point IR absorption cross sections for strong lines. For reaction products like HCl, CO, etc, we do not consider appropriate to include their IR integrated band intensities since they have been published elsewhere or were taken, as for methylglyoxal, from open databases.

Butane: Still surprised that the small yield of butane can be determined so well (to ~3% uncertainty) using the FTIR in the face of the overlapping bands from other species. Could you provide more insight into this. Perhaps add butane to Figure S9, and show an example spectral fit?

Authors' reply: As shown in the IR spectra below, although the absorption bands of butane overlap with butanone, it was possible to quantify it. In the upper panel, the residual spectrum obtained after irradiation and subtraction of unreacted 2MB is shown. The IR bands around 3000 cm^{-1} and 1500 cm^{-1} come from butane (reference spectrum in central panel). After subtracting the IR features from butane, the bands due to CO and butanone are still visible.

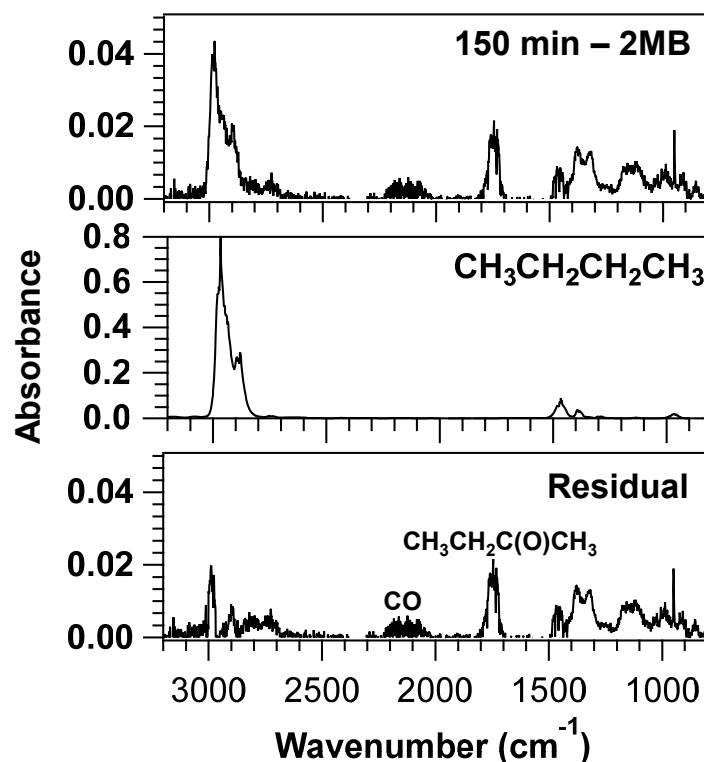


Figure C. FTIR spectra of a 2-methylbutanal/air mixture after 150 min of photolysis with the features of 2MB subtracted (top panel), butane (middle panel) and the residual spectrum after the subtraction of both (bottom panel).

However, to avoid the butanone interference in the quantification of butane we would like to insist that this procedure was performed as follows:

- 1) Subtraction of the IR features from the unreacted 2MB, focusing on the 2700 cm^{-1} and 2800 cm^{-1} bands.
- 2) Once 2MB was subtracted, the IR features of butanone were subtracted, focusing on the C=O stretching band at 1750 cm^{-1} .
- 3) Finally, the IR features of butane were subtracted of the resulting spectrum, focusing on the $2800\text{--}3000\text{ cm}^{-1}$ band.

As suggested by the reviewer, we have included in the supporting information a new figure (**Figure S10**) from which the yields of butane and butanone from 2MB photolysis were determined.

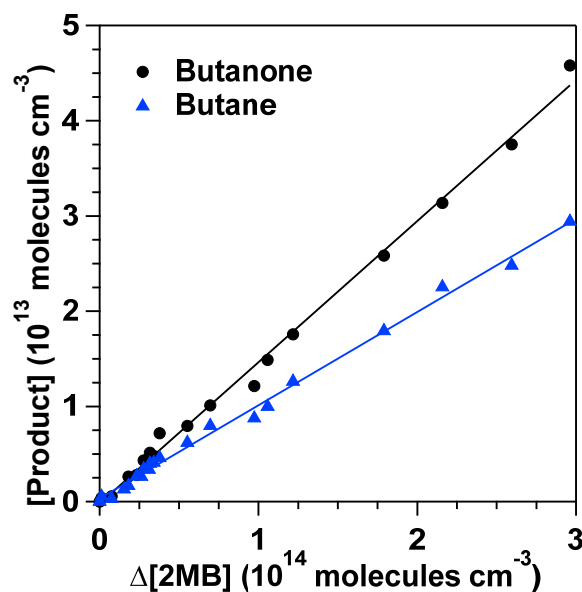


Figure S10. Plots to obtain the product yields in the 2MB photolysis determined by FTIR spectroscopy.

Autoxidation: The products identified (and proposed) by the authors are generally high volatility in nature, and unlikely to be able to account for particle nucleation and/or growth from very small clusters. It has recently been shown that certain autoxidation mechanisms can be quite fast and rapidly lead to low volatility materials which potentially could help explain the rapid onset of particle formation and growth. This question was posed to query the potential role for autoxidation in the formation of the observed SOA. Do the authors have additional ideas for which pathways lead to the SOA?

Authors' reply: We agree with the Referee: the products that were identified in this work were only volatile organic products, whereas low volatility organic compounds are needed for nucleation or coagulation of SOA. The autoxidation mechanism of RO₂ has been proposed to generate highly oxidized multi-functional molecules (HOMs) with a very low volatility. HOMs can, therefore, explain the formation of SOA. However, in this work it was impossible to measure the chemical composition of the formed particles, so we have no evidence to propose the mechanism that forms SOA in the 2MB + Cl reaction.

ROOH: These species are challenging to measure. They can rapidly decompose on various surfaces to other species. The initial questions regarding ROOH were trying to probe whether these species are stable in the employed apparatus and could be quantified by the instrumentation used. Even different instruments of the same type (e.g. PTRMS) can have significantly different efficiencies for decomposing ROOH (see e.g., <https://doi.org/10.1002/2014GL061919>). In addition, is it possible the lifetime of the ROOH over the glass surface is fairly short?

Authors' reply: As it was pointed out in the reply of the first revision, hydroperoxides were not detected by PTR-ToF-MS in this work. We agree with the Referee that, in addition to their reaction with Cl or their photolysis, hydroperoxides may have been decomposed on a surface, like metal parts of the PTR-ToF-MS through an homolytic peroxy bond cleavage catalysed by metals, as proposed by Rivera-Rios et al. (Geophys. Res. Lett. 41, 8645-8651, 2014). Given the lack of standards for the hydroperoxides that could be formed in the 2MB + Cl reaction, it is impossible to check if the surface decomposition observed by Rivera-Rios et al. might be happening in our system.

LN30-32: Suggest replacing 'diurnal' with 'daytime' here. While technically correct, some readers may interpret 'diurnal' to mean 'over 24 hrs' not simply 'when the sun is out'. Also, it may be simpler not to mention O₃ chemistry?

Authors' reply: These changes have been applied to the revised manuscript.

LN65-67: I understand this is historically how these observations have been reported. But, why not present 1-nm integrated cross-sections? Are these not be more useful? For many molecules (including this one) there probably is very little difference between single-point UV absorption cross-sections, and 1-nm integrated cross-sections, but for some species, those with highly structured cross-sections, this may not be the case. In addition, to understand what is meant by 'single point absorption cross-sections', one needs additional information regarding spectrometer optical resolution and data collection resolution—parameters which should be added to the manuscript.

Authors' reply: As pointed out by the reviewer, the 1-nm integrated UV absorption cross sections (S_{int} represented by a red line below) do not differ from the absolute

ones, since the UV spectrum of 2MB is not structured. In contrast to IR absorption cross sections, the UV absorption cross sections are usually reported as absolute values, not as S_{int} . This is mainly due to the use of some UV wavelengths (185 nm, 214 nm, or 254 nm) for quantification of reactants in kinetic measurements.

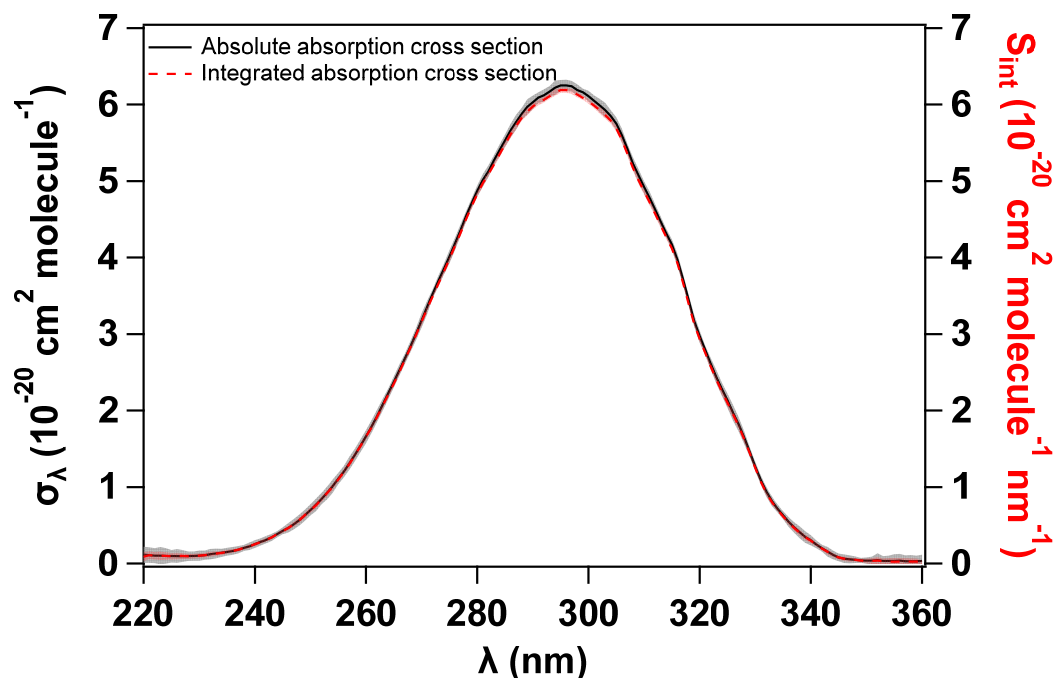


Figure D. Comparison between the absolute (black line) and integrated (red line) UV absorption cross sections.

Like for the IR absorption cross sections, we think that if needed by other researchers, they can easily use the tabulated UV absorption cross sections to obtain the integrated ones in a desired wavelength range. For that reason, we left Figure 2 as is.

Table S4: This addition is great. Can you specify what is represented by the uncertainties written here (+/- numbers). Is this total uncertainty, or just regression uncertainty? One or two sigma?

Authors' reply: The uncertainties included in Table S4 represent the same as the uncertainties presented throughout the manuscript: $\pm 2\sigma$ statistical, as it is stated in line 210 of the manuscript.