Review of "Atmospheric oxidation of α,β-unsaturated ketones: kinetics and mechanism of the OH radical reaction" by Illmann et al. (acp-2021-449)

General comments:

This paper describes the rate constants for the reactions of OH radicals with 3-methyl-3-penten-2-one and 4-methyl-3-penten-2-one and the reaction mechanism of these reactions. In addition, the rate constants for the reactions of Cl atoms with 3-methyl-3-penten-2-one and 4-methyl-3-penten-2-one were also investigated. The rate constants were determined by the relative rate method and the relative rates were obtained using three reference compounds for each reaction. The reactant and the products were monitored quantitatively by FTIR and the formation yields of the products were determined, considering their consumption and secondary formation processes. I think that this study was well-conducted and that the reliable data are presented. In addition, the paper is generally well-written. I recommend this paper to be published in Atmospheric Chemistry and Physics after the authors' consideration of my minor comments detailed below.

Specific comments:

(1) Page 11, Lines 300–301: Can the authors also discuss which carbon of the C=C double bond the OH radical attacks on preferably? Such the discussion will be useful for the comparison of the results of the product yields.

(2) Page 13, Lines 344–345: Did the authors confirmed that an epoxide is not formed in the ozonolysis of 2-methyl-3-buten-2-ol or that its yield is negligible?

(3) Page 18, Lines 445–446: Show what type of vibrational mode in 3-nitrooxybutan-2-ol the absorption bands at ~1660 cm^{-1}, ~1280 cm^{-1}, and ~850 cm^{-1} are. I want to know whether those bands are common in both 3-nitrooxybutan-2-ol and β-$RONO_2$ described in Figure 6.

(4) Page 22, Lines 563–564: The methyl group is electron-donating and the acetyl group is electron-withdrawing. So, I think that the OH radical attacks on C_β more preferably for 4M3P2 than 3M3P2. But we must consider steric effects, too. The argument in this sentence by the authors is probably based on the assumption of $\alpha_1 \gg \alpha_2$. I am not sure that the assumption is correct in the case of 4M3P2, as the authors mentioned that the branching fraction α_2 may be important for 4M3P2.

(5) Page 23, Line 569: I could not understand the meaning of "the stability of alkyl radicals". Explain it.

Technical comments:

(1) Page 2, Line42: Since the authors used "Tg" at Line 38, "10^5 t" is better to be expressed as "0.1 Tg" or "100 Gg".

(2) Page 2, Line42: Sifniades 2011 → Sifniades et al., 2011

(3) Page2, Line 42: “Hatch et al., 2017” is missing in References.

(4) Page 5, Line 145: Remove “-“ between “80-113 s” and “and 15-20 spectra”.

(5) Page 6, Line 173: The first “$k_{loss,ref.}$” should be “$k_{loss,ketone}$”.

(6) Page 9, Line 260: Add “IUPAC” in References.

(7) Page 17, Line 440: Add “HONO” and “HNO_3”, as mentioned in the text (Line 428).

(8) Page 22, Line 557: Fig 3, 6 → Figs. 3 and 6