

Anonymous Referee #1

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General comments

This material in this paper is within the scope of AMT. It reports on a laboratory study to quantify the reported difference in heterogeneous radical loss rates for HO₂ and RO₂ radicals and use it to design a radical amplifier to separate the signals due to these radicals. My concern is that this is a laboratory study and that no ambient measurements are reported. This would have been a huge addition to the paper.

As Referee#1 indicated, this paper does not report ambient measurements, but a laboratory study. The paper represents a proof of concept study in that it demonstrated, albeit in the laboratory, a new approach to selectively measure peroxy radicals by using a denuding method as well as highlighting data on the heterogeneous loss reactions of peroxy radicals.

Specific comments

Page 3294 line 15. There is no evidence that the photolysis of acetone at 185 nm only produces only methyl radicals. This path is less than 10% at 248nm (Rajakumar et al. 2008 J Photochem. Photobiol. A 199 336). Also here is no indication if the lamp is filtered, in which case photolysis of acetone can occur at 254 nm where the absorption cross section is much higher than at 185 nm. If acetyl and methyl radicals are both produced then the interpretation of the results is not so clear.

The low-pressure mercury lamp was not filtered, therefore the photolysis of acetone will occur mainly at 254 nm to produce CH₃O₂ and CH₃C(O)O₂ at about the same concentrations as per Referee#1 comment. Though removal efficiency of RO₂ might depend on the structure of R, CH₃O₂ and CH₃C(O)O₂ are thought to have comparably low removal efficiency values of 0.15 as shown in Fig.3. To clarify we have added the following sentence at page 3294 line 15:

The low-pressure mercury lamp was not filtered and the photolysis of acetone will occur mainly at 254 nm from its absorption cross section (Gierczak et al., 1998). The principle products are thought to be CH₃O₂ and CH₃C(O)O₂ at nearly equal concentrations ([CH₃O₂] : [CH₃C(O)O₂] ≈ 1.1 : 0.9) (Rajakumar et al., 2008).

Page 3299 line 3 we have added the following sentence:

Though the removal efficiency of RO₂ might depend on the structure of R, the average removal efficiency for both CH₃O₂ and CH₃C(O)O₂ radicals is 0.15 as shown in Fig.3

Page 3300 Eq 8 9. Figure 4 shows that α and β are functions of concentration. The authors should indicate how to use these equations to determine radical concentrations if these parameters are not

constant.

The constant removal efficiency of CH_3O_2 and $\text{CH}_3\text{C}(\text{O})\text{O}_2$ can be obtained at a concentration of ~ 150 ppt. According to this result, Eq 6, 7, 8 and 9 can be revised as follows:

$$S_{\text{HO}_2}[\text{HO}_2] + S_{\text{RO}_2}[\text{RO}_2] = \frac{I_{\text{blank}}}{C_{\text{humid}}}, \quad (6)$$

$$(1 - \alpha_{[\text{HO}_2]})S_{\text{HO}_2}[\text{HO}_2] + (1 - \beta)S_{\text{RO}_2}[\text{RO}_2] = \frac{I_{\text{removal}}}{C_{\text{humid}}}, \quad (7)$$

Then we can get each concentration of HO_2 and RO_2 as follows:

$$[\text{HO}_2] = \frac{(1 - \beta)I_{\text{blank}} - I_{\text{removal}}}{(\alpha_{[\text{HO}_2]} - \beta)S_{\text{HO}_2}C_{\text{humid}}}, \quad (8)$$

$$[\text{RO}_2] = \frac{(1 - \alpha_{[\text{HO}_2]})I_{\text{blank}} - I_{\text{removal}}}{(\beta - \alpha_{[\text{HO}_2]})S_{\text{RO}_2}C_{\text{humid}}}. \quad (9)$$

Page 3299 line 25 we have added the following sentence:

On the other hand, the constant removal efficiency for CH_3O_2 and $\text{CH}_3\text{C}(\text{O})\text{O}_2$ was obtained at a concentration of ~ 150 ppt.

Technical corrections

Page 3293 line 9. I think a reference to the original Cantrell and Stedman work should still be included.

As Referee#1 suggested, a reference of the original PERCA work of Cantrell and Stedman was added to revised manuscript. Page 3293 line 1 we have added the following sentence:

originated by Cantrell and Stedman [Cantrell and Stedman., 1982]

Page 3294 line 19. In reality there is no blank "cell".

Actually, the length of the blank cell was set so as to have the same residence time as the removal cell to confirm that radical loss was dominated by heterogeneous reactions. Page 3295 line 10 we have added the following sentence:

Additionally, the length of blank cell was set so as to have the same residence time as the removal cell to confirm heterogeneous radical loss reaction was dominant.

Page 3295. Do not mix metric and imperial units

Imperial units were changed to metric.

Page 3296 line 6. The laser is different than that in Fig 1

Fig. 1 is correct. Manuscript was revised.

Page 3297 Eq 2. The use of I_{dec} is confusing. Since I_{blank} refers to the blank path, then it should be called I_{removal} to be consistent.

As Referee#1 suggested, all of I_{dec} was changed to I_{removal} .

Page 3297 line 5. Remove (I_{HO_2})

(I_{HO_2}) was removed in the revised manuscript.

Page 3300 Eq6. The casual reader would not realize that C_{humid} is independent of the radical measured. This should be clarified.

As Referee#1 suggested, more information on C_{humid} was added. Page 3300 line 16 we have added the following sentence:

The factor C_{humid} , i.e. the variation of the chain length only with relative humidity independent of the radical concentration, has been determined.