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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Rate coefficients for the reaction of methylglyoxal (CH_3COCHO) with OH and NO_2 and glyoxal $(HCO)_2$ with NO_3" *by* R. K. Talukdar et al.

Anonymous Referee #1

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OVERALL

The kinetic measurements from this laboratory are always of the highest quality, which is in part due to the range of experimental diagnostics employed. Therefore I'm confident that the reported rate constants in this study are reliable.

If the question is has these measurements improved the uncertainties in the atmospheric processing of methyl glyoxal, then the answer is not so clear as it is the products of the reaction where the uncertainty lies, not the removal rate coefficient. The products of the OH + methyl glyoxal reaction was addressed in the study of Baeza-Romero, where it was shown that at low pressures 50 % of acetyl product further

dissociates to CH3 + CO. Rate theory calculations were used to extrapolate to atmospheric pressure, and it was predicted that $\sim$ 40% was still dissociating to CH3 + CO. This extrapolation assumed that the energy of the reaction was statistically distributed, but there are questions on the validity of this assumption. The fact that in this paper the products have been assumed to be 100 % acetyl leads me to conclude that the paper by Baeza-Romero was not properly read. This needs to be discussed, especially in the discussion where PAN formation from acetyl is discussed. In fact, the Boulder laboratory has a cavity ring down detection system for the acetyl radical, so the logical step would have been to use this method to assign the acetyl yield from the OH + methyl glyoxal reaction.

LINE BY LINE COMMENTS

18212 Line 25: probably need to point out that the excess energy from reaction 1a is enough to dissociate CH3COCO to CH3CO, and there is still enough energy to dissociate further to CH3 + CO

18214 Line 23: Are the products of the reaction more of an issue than improving the errors in the rate constants?

18214 Line 28: are there any estimates for processing methylglyoxal/glyoxal at night? Is aerosol processing likely to be most significant at night time?

18217, line 25. It should be the Beer-Lambert law, not Beer's law

18219, line 14. How do you test that passing from the reaction flow tube to the ionization region that time is not distorted. Errors in time?

18219, line 21. Could you indicate the value of kw? It appears to be very low, i.e. almost no loss of NO3 to the walls or with NO2. From Figure 5, k'3 ranges from 0.3 – 0.7 s-1, which represents only a very small change in NO3 over 85 ms. Can you accurately measure this small change in NO3, i.e. can you state how precisely you can measure NO3 using the CIMS system.

18222, line 24. The OH yields form acetyl + O2 in either He or N2 can be readily calculated from the paper: S. A. Carr, D. R. Glowacki, C.-H. Liang, M. T. Baeza-Romero, M. A.Blitz, M. J. Pilling, and P. W. Seakins, J. Phys. Chem. A 115, 1069 (2011). This will give a quantitative guide to the amount of recycled OH.

18223, line 8. Where does the 13% from reaction 10 come from? Reference.

18226, line 20. Canonical variational transition state theory assumes that the reaction follows the potential energy surface. However, reactions do not follow the potential energy surface (PES) as collisions are required to remove the starting energy of the reactants if it is to follow the PES. This is especially the case when there is no overall barrier to reaction. Therefore cVTST is not really quantitative, so it is fortuitous that they predict the experimental rate constant. A more rigorous way to calculate such a rate constant is given by E. E. Greenwald, S. W. North, Y. Georgievskii, S. J. Klippenstein, J. Phys. Chem. A 2005, 109, 6031-6044.

18227. While the Galano paper provides insight into the mechanism driving the negative T dependence of the reaction, as noted above, it is not quantitative in determining rate coefficients as cVTST is used.

There appears to be a major point that was not picked up in the paper by Baeza-Romero. In the reaction OH + methyl glyoxal Baeza-Romero observed acetyl to be a significant product of the reaction, and this was also identified in the present study by measuring a smaller rate constant when O2 was added at 50 Torr. In the paper by Baeza-Romero, they quantified this channel and concluded that $\sim$ 50% was further dissociating to CH3 + CO. This was modelled, using a number of assumptions, and predicted that 40% CH3 + CO products is still occurring at atmospheric pressure. In the atmospheric implications, it was assumed that the products are 100% acetyl, with no further dissociation to CH3 + CO. This would appear to be a more important aspect of the reaction than the improvement of the rate coefficient from this study. Quantifying the acetyl yield from the reaction is something that could be done in the Boulder

laboratories as there is a cavity ring down setup to detect the acetyl radical.

18228, line 8. If the wall losses was 1-2 s-1 can you reliably assign rate constants between 0.3 – 0.7 s-1? This must be even harder when the change in the NO3 from reaction of only a few %.

18230, line 8. Is there any experimental evidence that NO3 reacts with acetone, i.e. is reference Boyd et al. an upper limit?

In general, if NO3 is reacting with glyoxal and methyl glyoxal by abstracting the weakest H, i.e the aldehydic H, then it would appear that the products of reaction are HCO + CO + HNO3 and CH3CO + CO + HNO3, respectively. In the flow tube experiment would it have been possible to detect HCO (glyoxal) or OH by adding O2 (methyl glyoxal) or HNO3 in both reactions using the CIMS detector.

18232, line 6. It is assumed that the product of the reaction is $\sim$100% acetyl, but the study of Baeza-Romero predicts that 40% of the acetyl decomposes further to CH3 + CO. Please comment.

18238. Should Table 1 go into the supplementary?

18242, Figure 1. Should this diagram be amended to taken into account the potential mechanism of Baeza-Romero: OH + CH3COCHO -> CH3 + CO + H2O. If there is little evidence that CH3C(O)CO has a significant lifetime should this be included in the figure?

18246, Figure 5. Regarding the errors in the measurements would it be better to plot k' versus glyoxal?

18225, line 2. Should be 10(13). 18225, line 3. Should be 10(12).

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 18211, 2011.