**Atmospheric
Chemistry
and Physics
Discussions**

# *Interactive comment on* "Rate coefficients for the reaction of methylglyoxal (CH$_3$COCHO) with OH and NO$_2$ and glyoxal (HCO)$_2$ with NO$_3$" *by* R. K. Talukdar et al.

**R. K. Talukdar et al.**

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Dear Editor: 20 September 2011

Re: Title: Rate coefficients for the reaction of Methylglyoxal (CH3COCHO) with OH and NO3 and Glyoxal (HCO)2 with NO3 Author(s): R. K. Talukdar, L. Zhu, K. J. Feierabend, and J. B. Burkholder MS No.: acp-2011-456

Here, we are submitting the revised manuscript. The manuscript has improved by adding the reviewers' comments. The main reviewer comments were not focused on the body of our experimental work, but were primarily concerned with a more complete description of previous studies and specific detection of product yields. The main fo-

cus of our paper was to accurately measure the rate coefficients of OH reaction with methylglyoxal and the NO3 rate coefficients with glyoxal and methylglyoxal, thereby defining the lifetime and the degradation pathways of these compounds in the atmosphere. We have addressed the reviewers comments as best as possible, but in several cases, such as methylglyoxal and glyoxal deposition losses and OH production in the CH3CO + O2 reaction, these are active areas of research and therefore could not be resolved in the present paper. The reviews, our responses to the reviewer comments, and the actions taken are given on the subsequent pages. We hope the manuscript is acceptable for publication in ACP.

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We thank the referees for their valuable time and effort to evaluate the manuscript. Here we have responded point by point to both referees' comments. Several of the comments are, however, related and have been combined in our response.

We like to bring to the attention of referee and editor that there is a typo in the title. "NO2" should have been "NO3".

Referee #1: 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 ∼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.

Response: The uncertainty in the product yield in the OH + methylglyoxal reaction are at present in doubt. The product yield from this reaction will impact the model calculated PAN yield. In our ACPD paper we did not adequately address this uncertainty. We have made changes to the text to reflect the uncertainty in PAN production from methylglyoxal in the atmosphere. The measurement of reaction product yields was not included as part of the present study. In the atmospheric implication section we have mentioned that experimental measurements to quantify the PAN yield under atmospheric conditions would be useful. Cavity ring-down experiments as suggested by the referee are another possible way to investigate the $CH_3CO$ yield, but were not included as part of the present work, which was focused on reducing the uncertainty of OH rate coefficients and extending the experimental data to lower temperatures, and measure rate coefficients of the $NO_3$ reactions with glyoxal and methylglyoxal. Action taken: We have made changes to the text in several places. (1) In the third paragraph just below the reaction channels of the Introduction, we added "$CH_3COCO$ radical formed in channels 1a and 1d spontaneously dissociates to $CH_3CO$ and CO in <15 $\mu$s (Green et al., 1990). $CH_3CO$ radical from channel 1a has sufficient energy to dissociate further to $CH_3$ and CO (Baeza-Romero et al., 2007)."

Second paragraph in the atmospheric implications section: "$CH_3CO$ radical has sufficient energy and as much as 40% may dissociate further to $CH_3$ and CO even under atmospheric condition, thereby potentially reducing the effective yield of $CH_3CO$ (Baeza-Romero et al., 2007)." And 8 line down from here "the overall yield of $CH_3CO$ radical" End of second paragraph in Atmospheric Implications section "A direct mea-

surement of molecular yields in the degradation of methylglyoxal under atmospheric conditions is needed."

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 Response: Referee perhaps meant 18213 Line 25. We agree with the referee regarding the possibility of further dissociation of CH3CO to CH3 + CO although it is not clear to what extent it occurs under atmospheric condition. Action taken: We have made changes to the text just below channels 2a-d "CH3COCO radical formed in channels 1a and 1d spontaneously dissociates to CH3CO and CO in <15 $\mu$s (Green et al., 1990). CH3CO radical from channel 1a has sufficient energy to dissociate further to CH3 and CO."

18214 Line 23: Are the products of the reaction more of an issue than improving the errors in the rate constants? Response: Quantifying the various loss processes and the reaction products are both important to determine the fate and impact of methylglyoxal on the atmosphere. The focus of the present work was to reduce the uncertainty in OH rate coefficients and measurements of NO3 rate coefficients. We already said in the last sentence, 3rd paragraph in the Introduction " It is important to quantify the degradation pathways to fully evaluate the impact of methylglyoxal on tropospheric chemistry." Action taken: None

18214 Line 28: are there any estimates for processing methylglyoxal/glyoxal at night? Is aerosol processing likely to be most significant at night time? Response: No specific estimates of the nighttime loss processes are currently available in the literature. Dry and wet deposition may represent nighttime loss processes under some conditions but requires further study. The present work has shown that nightitme loss due to the NO3 reaction to be negligible. Action taken: We have added further discussion on this point in atmospheric implication section in response to referee # 2.

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

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law" has been changed to "Beer-Lambert 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? Response: Rate coefficients were measured under different flow and pressure conditions. No problems were identified. In flow tube kinetics the relative reaction distance is measured and reaction time is calculated from the calculated flow velocities to better than 2%. The systematic errors in flow velocities and the measured NO3 rate coefficients are therefore small and the conclusions from this study are not significantly impacted. Action taken: None

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. Response: kw was $0.2 \pm 0.05$ s-1. For NO3, kw values were in the range 0.2-0.5 s-1, in figure 5. Even with the lowest k' of 0.3 s-1 for reaction of NO3 with glyoxal, the change in [NO3] during 85 ms reaction time was ∼2.5%. With a S/N ratio of ∼1000 changes in [NO3] of less than 1% could be measured. Action taken: We have added in the experimental section of flow-tube CIMS: "With a signal-to-noise ratio of ∼1000 and a detection sensitivity of $\sim 2 \times 10^8$ molecule cm-3 for one integration, changes in [NO3] of less than 1% could be measured."

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. Response: We thank the referee for mentioning this work, which we are familiar with. We reported our results in connection with the low-pressure kinetics measurements in He and the problems associated with it. The present kinetic measurements were performed under conditions where recycled OH was not important and did not influence the determination of the reaction rate coefficient. It is outside the scope of our work to discuss further the OH

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yields in the acetyl + O2 reaction. Action taken: None

18223, line 8. Where does the 13% from reaction 10 come from? Reference. Response: The ~13% OH yield was obtained from the measured change in the pseudo-first-order rate coefficient in 50 Torr He measured following the addition of O2 to the reaction mixture. We have shown in Gas Kinetics Meeting, 2006 held in Orleans, France, that in excess O2, when the first order rate coefficients for the regeneration of OH » k′(OH + R), then it can be shown that fractional decrease in the measured rate coefficient ≈ yield of OH. We have referred the Gas Kinetics Meeting, 2006. Action taken: We have referred the Gas Kinetics Meeting, 2006.

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. Response: Greenwald et al. have presented a more sophisticated level of theory but did not calculate the OH + methylglyoxal reaction rate constant. Therefore, we have compared our temperature dependent experimental data with the only available theoretical value in the literature. Action taken: None

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 ~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. Response: A direct experimental determination of the product yields under atmospheric conditions are indeed needed to better understand the impact of methylglyoxal oxidation with the oxidation capacity of the atmosphere. However, such work was not within the scope of the current project. We have modified figure 1 and the text to better represent the uncertainty in the product yields. Action taken: We have modified figure 1 to include the possible dissociation of CH3CO. We have made changes in the text to include the uncertainty in the CH3CO yield in reaction 1 in the atmospheric implications section. Second paragraph in the atmospheric implications section: "CH3CO radical has sufficient energy and as much as 40% may dissociate further to CH3 and CO even under atmospheric condition, thereby potentially reducing the effective yield of CH3CO (Baeza-Romero et al., 2007)." And 14 line down from the previous sentence ". . ..the overall yield of CH3CO 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 %. Response: We have corrected the text. Wall loss was $0.2 \pm 0.05$ s-1. Please see the previous response for the first part (18219, line 21). Action taken: We have added in the experimental section on flow tube kinetics, 2nd sentence from the bottom: "(typically in the range: $\sim 0.2 - 0.5$ s-1)"

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 +

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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. Response: There is no evidence of NO3 reacting with acetone and Boyd's number for acetone was an upper limit. We did not attempt to detect the products of the NO3 reactions in our determination of the rate coefficients. HNO3 detection, however, would be complicated as there is always some HNO3 present from NO3 source, which was much more than that could be produced in NO3 + glyoxal or methylglyoxal reaction. We agree that the most likely reaction be abstraction of the aldehydic H-atom. Action taken: None

18232, line 6. It is assumed that the product of the reaction is ∼100% acetyl, but the study of Baeza-Romero predicts that 40% of the acetyl decomposes further to CH3 + CO. Please comment. Response: Please see previous response on this topic 18238. Should Table 1 go into the supplementary? Response: We choose to keep Table 1 in the body of the paper. After our paper was published in ACPD, a paper by Profeta et al. was accepted in JPCA (Profeta, L. T. M., Sams, R. L., Johnson, T. J., and Williams, S. D.: Quantitative Infrared Intensity Studies of Vapor-Phase Glyoxal, Methylglyoxal, and 2,3-Butanedione (Diacetyl) with Vibrational Assignments, J. Phys. Chem. A, 115, 9886–9900, 10.1021/jp204532x, 2011). The IR cross sections are in excellent agreement with their measurements. We have referenced their work in the text. (their note added in proof: "Subsequent to this paper being accepted, Talukdar et al. published online a kinetics study of methylglyoxal containing a quantitative IR spectrum at 1 cm_1 resolution. Their results agree very well with the present work, to approximately the 3% level for the absolute intensities. Please see R. K. Talukdar, L. Zhu, K. J. Feierabend, and J. B. Burkholder, "Rate coefficients for the reaction of methylglyoxal (CH3COCHO) with OH and NO2 and glyoxal (HCO)2 with NO3," Atmos. Chem. Phys. Discuss. 2011, 11, 18211_18248.)." Action taken: We added at the end of the Absorption cross-section measurements section "After our ACPD paper was published, an IR absorption study of several dicarbonyls was published (Profeta et al., 2011). The agreement in absolute intensities between their results and the present

work is excellent (within 3%)."

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? Response: It is not clear whether this also holds true for the NO3 reaction as the reaction enthalpy is a lot lower ($\Delta$H = -16.7 kcal/mol compared to -27.1 for the OH reaction). Therefore, we chose to keep the CH3C(O)CO radical in the diagram. Action taken: We have modified Figure 1 to include the dissociation of CH3CO to CH3 + CO.

18246, Figure 5. Regarding the errors in the measurements would it be better to plot k' versus glyoxal? Response: We do not understand the comment, as that is what is plotted in figure 5. Action taken: None

18225, line 2. Should be 10(13). 18225, line 3. Should be 10(12). Response: Rate coefficient values quoted in the text are correct and appropriate references are given. Action taken: None

Referee #2: 1. The manuscript discusses OH and NO3 chemistry, which typically are day and night. I am not certain of this, but I could imagine that it might make sense to split figure 1 into day- and night-time or address this point in some other manner. Response: The NO3 reaction is predominantly a nighttime process. Action taken: We have modified the diagram to clarify day/night loss processes and to reflect uncertainty of CH3CO yield in channel 1a.

2. The comments of anonymous referee #1 with respect to the fate of the CH3COCO radical are pertinent to this and should be addressed. Response: We addressed the comments of referee #1 and made changes accordingly.

3. The authors do not discuss dry deposition much. However, especially at high relative humidity I would not be surprised at all if ground-level measurements could be strongly affected by this, in particular at night in stable night-time atmospheres. Another impor-

tant point worth mentioning is the work by Karl et al. 2010 that showed that deposition can be much higher than expected. It is likely that for the alpha-dicarbonyls photolysis and/or reaction with OH will remain the dominant term, but I believe including all terms that can affect them is important. Response: Dry deposition losses for the fast reacting atmospheric species are not well known and often ignored. The modeling paper of Fu et al. uses low dry deposition rates compared to the uptake on cloud and aerosols. Recently, Karl et al. established from their laboratory and field measurements that dry deposition could be a significant contributor to overall process for oxygenated VOCs, including glyoxal and methylglyoxal. They showed that dry deposition fluxes of glyoxal and methylglyoxal increased by ∼+100% and ∼17% respectively (Karl et al.). Wet deposition fluxes decreased for methylglyoxal by <10% and glyoxal did not exhibit any change in wet deposition fluxes. However, the overall global deposition lifetime was not reported in the paper. Action taken: We have modified the text to include the possible effect of dry deposition on the lifetime of glyoxal and methylglyoxal. Third sentence in the Atmospheric Implications section reads: "Dry deposition losses are not well defined and often ignored. Recently, Karl et al. (Karl et al., 2010) estimated, based on their laboratory and field measurements, and transport modeling, that the dry deposition of glyoxal and methylglyoxal can increase by ∼100% and ∼20% respectively compared to the previous estimates (Goldstein and Galbally, 2007; Hallquist et al., 2009; Zhang et al., 2002), which were used by Fu et al. In addition, ground-level measurements of oxygenated VOCs, particularly at night under high relative humidity scenarios, could be significantly impacted because of dry deposition. Dry and wet deposition, and the uptake on clouds and aerosols would be a function of location and likely to be significant nighttime loss processes." and the last two lines of the 1st para of Atmospheric Implications: "Including dry deposition would decrease the lifetime of both dicarbonyls. However, their atmospheric loss would still be dominated by UV photolysis, OH reaction and the uptake on clouds and aerosols."

4. The authors state that the reaction of MGLY+OH is HOx neutral (p.18232 line 3) and go on to discuss PAN. The PAN formation is a net radical loss (termination) as a OH

and NO2 radical are lost. Clearly, PAN gets destroyed again to reform these but if this is what the authors mean an important point is that for a specific location the reaction of MGLY+OH could be a radical sink due to export of longer-lived PAN. This aspect could be emphasized more and play into the implications of the manuscript. Response: We agree with the referee's suggestion. Action taken: We have modified the text in the middle of the second paragraph of the Atmospheric Implications section as follows "The loss of methylglyoxal due to the OH reaction leads to a null HOx production cycle if the products of the reaction do not leave the region. The OH reaction with methylglyoxal and the subsequent formation of PAN lead to the local loss of OH and NO2 radicals. The transport of PAN to remote areas represents a HOx and NO2 source. Thus, the OH reaction with methylglyoxal acts as local radical sink and remote source of HOx."

5. I think it could be useful to include formaldehyde in the comparison of GLY/MGLY with acetaldehyde and acetone+NO3. Response: We agree with the referee's suggestion. Action taken: We have included NO3 + HCHO in table 4 and added text in the "Comparison of NO3 rate coefficients" section (1st paragraph) "…., formaldehyde (HCHO),.." 3rd paragraph. "However, OH reaction rate coefficient of glyoxal compares well with that for formaldehyde (HCHO) and so does their NO3 rate coefficients at room temperature." "The estimated C-H bond energies of the -C(O)H group in glyoxal, methylglyoxal, formaldehyde, and acetaldehyde are 84.8 (Feierabend et al., 2009), 74, 88.6 and 89.4 kcal mol 1, respectively (Sander et al., 2006; Galano et al., 2004)."

6. The work of Kroll et al. 2005 should be added and contrasted to the work of Fu et al. as Kroll et al. found no measurable uptake of MGLY on ammonium sulfate aerosol. I believe this is required for balance. It should also be clarified whether the uptake of Fu et al. implied cloud processing (i.e. chemistry) or simply partitioning. Response: We do not quite understand why there is such a large discrepancy in the uptake number. Henry's law constant of MGLY is $\sim 2500$. Even if there were just a solvation without any reaction, uptake on cloud and aerosol would be large. We believe because of the low RH (50-55%), the uptake could be very low. However, Fu et al. calculations of uptake

on clouds were much higher than that would be based on the uptake reported by Kroll et al. on ammonium sulfate aerosols. Action taken: We pointed out and discussed this issue. "On the other hand, Kroll et al. did not observe a net growth of ammonium sulfate aerosols in the presence of methylglyoxal at ~50% relative humidity (Kroll et al., 2005). This is contrary to growth of particles in the presence of other dicarbonyls (Jang et al., 2003; Jang et al., 2005; Jang and Kamens, 2001). The large discrepancy could be due to the low RH (50-55%) used in Kroll et al. study leading to low uptake."

Technical Comments: Table 3 contains the explanation of the acronym MS, but I did not see MS show up anywhere in the table. Response: Referee is correct! Action taken: Deleted the acronym MS

Figure 2: How much are the OH profiles offset. Response: Offsets vary from profile to profile (between 200-600 units)

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C9156/2011/acpd-11-C9156-2011-supplement.pdf

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