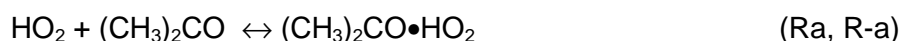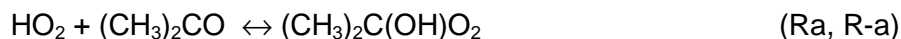Dear Prof. Donahue,

We thank all of the referees for their helpful and constructive comments. The subject matter is clearly rather complex; our understanding of the chemistry involved has certainly deepened following this review process. Particularly important issues raised by referees Peeters and Tyndall regarded the non-reactive complexing of HO_2 to both $CH_3C(O)CH_3$ (Ra, R-a) and CH_3OH (Rb,R-b) which were neglected as our data analysis focused on (R1,R-1)

$$HO_2 + (CH_3)_2CO \leftrightarrow (CH_3)_2C(OH)O_2 \qquad\qquad (Ra, R\text{-}a)$$

$$HO_2 + (CH_3)_2CO \leftrightarrow (CH_3)_2CO\bullet HO_2 \qquad\qquad (Ra, R\text{-}a)$$

$$HO_2 + CH_3OH \leftrightarrow CH_3OH\bullet HO_2 \qquad\qquad (Rb, R\text{-}b)$$

We have subsequently conducted several simulations which reveal that both processes (Ra) and (Rb) reduce our sensitivity to the reaction of interest (R1) at 207 K where we observe evidence for reaction. However, these simulations indicate there is little impact at 228 K where our observations of little / no HO_2-$CH_3C(O)CH_3$ interaction conflict with the theoretical predictions of Hermans et al. The discussion section of our manuscript will be revised for publication in ACP, particularly as regards uncertainties in derived values of K_1. Three different scenarios will be considered:

Scenario 1 ((R1) included but with no complexes of HO_2 with $CH_3C(O)CH_3$ or CH_3OH). Essentially the interpretation of data that was presented in ACPD. A slight modification to include the experimentally verified complex formation with CH_3OH (Rb) forms the basis for **scenario 1.1**, though our simulations indicate this impacts little on the derived values of k_1 and K_1.

Scenario 2 (complexes of HO_2 with $CH_3C(O)CH_3$ (Ra) and CH_3OH (Rb) included but without Hermans (R1) chemistry). The simulations indicate that we are essentially blind to (Ra) and (Rb) assuming efficient reactions of the complexes with NO to form OH. **Scenario 2.1** considers the impact of complex + NO to form products other than OH (eg. $CH_3C(O)CH_3$ + HNO_3).

Scenario 3 ((R1), (Ra) and (Rb) included using published values for equilibrium constants) preliminary simulations indicate this scenario is consistent with observations at 207 K but not at 228 K. Modified version **scenario 3.1** considers how much larger values of K_a are needed at the higher temperatures to bring the observations in to line with Hermans calculations of (R1).

As outlined above, the conclusions of the paper remain largely unchanged by these developments. A number of technical corrections were also suggested, all of which are reasonable and have been attended to with a view to production of a revised manuscript (see the table below for details).

Specific Comments from Referees		Our Response (in blue)
From J. Peeters (Referee)		
The authors have performed an experimental investigation of the reaction between HO2 radicals and acetone at low temperatures of 207 - 228 K and reduced pressures of 25 - 85 Torr, essentially based on measuring the OH resulting from the competition between (i) the sequence HO2 + CH3C(O)CH3 <-> (CH3)2C(OH)OO (R1, reversible; k_1 and k_{-1}) followed by (CH3)2C(OH)OO + NO → products (k2), and (ii) the well known reaction HO2 + NO→OH + NO2 (k8). The OH was monitored by LIF and calibration was achieved on basis of the kinetically well characterized reaction system in absence of acetone. The experimental		

results, obtained using proven methodologies, are of high quality, and the lower-limit k1 data that could be derived directly are by themselves of much value, showing that the reaction does indeed occur at these low temperatures at rates of at least 1 x 10(-12) cm3 s-1 at T _ 210 K and 25 Torr.

However, the more involved interpretation of the experimental data in terms of both k1 and k-1 (or K1) is not straightforward (see Specific Comments, below), and more importantly, two aspects of reaction (R1), with a large impact on the chemistry as detailed in the Specific Comments below, were not taken into account. Thus, though the paper shows convincingly that reaction (R1) does occur, the derived k-1(T) and equilibrium constant K1(T) data are both questionable, and the conclusion of the authors that the HO2 initiated oxidation of acetone and formation of acetic acid thereby is not significant in the tropopause appears therefore insufficiently substantiated. The interpretation of the data should therefore be re-addressed, in the light of the particular aspects of reaction (R1) detailed below.

The interpretation was certainly not as straightforward as depicted in the ACPD article. Reanalysis has shown that whilst these experiments were not as sensitive to K_1 as previously thought, the lack of reaction observed at T = 228 K is still not consistent with the findings of Hermans et al.

Specific Comments 1. First, it should be noted that the k-1(T) and equilibrium constant K1(T) results obtained by the authors appear rather unusual in the light of the experimental data for the analogous reactions of HO2 with HCHO and CH3CHO and the reverse reactions. The reported k-1(T) for (CH3)2C(OH)OO decomposition imply a very high k-1(300 K) of around 2x10(6) s-1. When comparing this result to the experimental values of 175 s-1 for H2C(OH)OO (Veyret et al., 1989) and 1900 s-1 for CH3CH(OH)OO (Tomas et al., 2001), the carbonyl-stabilizing inductive effect of the second CH3 group seems a hundred times stronger than that of the first CH3 substituent, which is definitely not in keeping with group additivity concepts.

Whilst the impact of (Ra) and (Rb) is moderate at around 207 - 228 K, a larger error may have resulted from their omission when extrapolating to 298 K, beyond the range of experimental data. This issue can be addressed in the revised manuscript in the discussion of scenario 3. Note also that we used the theoretical entropy term from Hermans et al. in constructing a "3rd-law" fit in Figure 3; this is not appropriate at least as regards scenario 2 (see above).

Further, from the reported K1(T) results, the stability of (CH3)2C(OH)OO with respect to the reactants appears to be 11 kJ mol-1 less than the 59 _ 2 kJ mol-1 computed at various high-levels of theory by Hermans et al., 2005, whereas the stabilities computed in that same paper at the same levels of theory for the two analogous _-OH-peroxys CH3CH(OH)OO and H2C(OH)OO were shown to agree with experiment within 2 kJ mol-1. This gives reason to question the more involved interpretation of the [OH] data in presence/absence of acetone in terms of both k1 and k-1.

There appears to be some doubt as to whether theory- experiment agreement for other chemical systems is relevant, with Referee 2 commenting as follows:
"Page 16750, lines 5-10: It is not clear or true that the agreement of theoretical calculations for other reaction systems should give you confidence in the Hermans et al. (2004) calculations."

2. The apparent rate constant that can be derived from the measured reduction of [OH] upon acetone addition is essentially k1/(1 + k-1/k2[NO]), or K1/(1/k-1 + 1/k2[NO]), and hence k1 and k-1 (or k1 and K1) could not be obtained independently from these experiments. The authors opted for adopting the theoretically predicted k1 of Hermans et al. 2004, and so deriving k-1 (and hence K1) from the observed [OH] reduction upon acetone addition. This by itself was not the best choice, since the theoretical k1 of Hermans et al. 2004 (as all the k in that paper and likewise in Hermans et al. 2005) are TST-based and therefore by definition high-pressure limit values, whereas the reaction

in question, through a stable pre-reactive complex (PRC) and over a submerged barrier, will necessarily show pressure-dependence, while the experimental pressures are quite low. Moreover, equilibrium constants, besides being independent of pressure, can in general be predicted (much) more accurately than rate coefficients; therefore, a better choice would have been to adopt the theoretical K1 of Hermans et al. 2005,
in which paper the stability of the _-OH-peroxy at hand was verified at higher levels
of theory compared to the 2004 paper, and the rate coefficients at issue here were accordingly upgraded.

We used the theoretical k_1 values since these were consistent with our observation of a substantial k_1 at 207 K. By contrast the theoretical values of K_1(228 K) were simply not consistent with experimental observations, unless a much larger than published value of K_a is used to remove our sensitivity to (R1) – see below. We take the point however that when considering the theory alone calculated equilibrium constants (K) are normally more robust than calculated rate coefficients (k).

3. As to the pressure-dependence of reaction (R1), the rate of prompt redissociation of the nascent chemically activated PRCy formed at 210-230 K can be estimated at roughly kred(Eav = 8 kJ/mol) _ 3x10(9) s-1, such that at 25 and 85 Torr, collisional stabilization, with _scZLJ[M] of _5x10(7) s-1 and _1.5x10(8) s-1, respectively, is too slow and hence product formation occurs mainly through the nascent, activated PRCy, meaning that the reaction is in its low-P limit. The forward kf(Eav = 8 kJ/mol) rate to form the product is estimated at about 2x10(7) s-1, i.e. 100 times slower than redis- sociation; both these rates are estimated here from the data in Hermans et al. 2005 and their available Supporting Information. (See Note on rates estimated in these comments, below). That higher pressures should increase the product formation rate (i.e. the effective k1) substantially, is readily seen: PRC(y) that are brought just below the reactants level by collisions can no longer redissociate promptly, but still promptly yield the product as the submerged transition state lies 11 kJ mol-1 below the reactants (see Hermans et al. 2005 for the energetics). The pressure effect at these low T should be pronounced; assuming an HO2-acetone capture rate kcapt = 10(-10) cm3 s-1, the low-P k1 is estimated at barely 10(-12) cm3 s-1, i.e. substantially lower than the upgraded high-P limit k1,1(207 K) = 5.8x10(-12) cm3 s-1 and k1,1(228 K) = 3.0x10(-12) cm3 s-1 predicted by Hermans et al. 2005.

Given the combined uncertainties in the theoretical calculations and these rather indirect experiments we regarded the (lower limit) value of k_1 reported here at 207 K and the equivalent calculation from Hermans et al. to be in good agreement (and contrasting with the predictions of Cours et al. of a slow $k_1 \approx 10^{-16}$ cm^3 molecule^{-1} s^{-1}). Agreed, experiments were not conducted in the high pressure regime. Nonetheless, we do obtain evidence for (R1) at 207 K, ie. experiments were conducted at high enough P to be sensitive to k_1.
At issue however is why we see little or no evidence for (R1) at slightly higher T (and higher P). It seems unlikely that a change of just 21 K (whilst increasing P by a factor of >3) would cause an order-of-magnitude lowering of k_1. We remain convinced that a substantial increase in k_1 between 207 and 228 K is a more plausible explanation.

4. Equally important, but not considered by the authors, is that at these low T and high [acetone] around 10(15) cm-3, the bulk of the HO2 can be expected to be sequestered in the very stable H-bonded OOH—O=C(CH3)2 PRC complex, in thermal equilibrium with acetone and free HO2. The HO2 + CH3C(O)CH3 $ OOH—O=C(CH3)2 complexation (Kcompl) was first described by Aloisio and Francisco 2000 at B3LYP level, while Hermans et al. 2005 computed an even slightly higher complex stability of 41_4 kJ mol-1 at several higher levels of theory, giving also the vibration/rotation parameters in Supporting Information (SI). Of much impact on the issue at hand are the magnitude of Kcompl(T) and the timescale to attain the equilibrium. Kcompl(200-230 K) is large because the complex is stable but at the same time quite "loose" and hence exhibits a high density of states and high partition function on account of the quasi-free internal rotation of the terminal hydroperoxy-O about the O-H—O= axis. The harmonicoscillation-approximation of Gaussian attributes a "vibration frequency" of 60 cm-1 to this mode (see SI Hermans et al. 2005), but

this results merely from a small dip in the (otherwise flat) V(_) internal rotation potential, at a dihedral angle where the terminal hydroperoxy-O is close to the nearest methyl-H (but still 2.6 A distant); the 207 K partition function for this quasi-free internal rotation mode is estimated at about 20, i.e. much higher than the HOA value of 2.9. As earlier reported by Aloisio and Fran- cisco, two other new modes of the complex (Gaussian "frequencies 83 and 157 cm-1" of Hermans et al.) are hindered internal rotations, which together can put the partition function another factor of _3 above the HOA approximation. Thus, Kcompl(T) is roughly estimated at about 3x10(-14) cm3 at 207 K and 5x10(-15) cm3 at 228 K, with a probable error of a factor of 10. Given the experimental [acetone] of order 10(15) cm-3, this implies that at equilibrium the bulk of the HO2 (some 80% to well over 90%) can be tied up in the thermal OOH—O=C(CH3)2 complex.

The equilibrium (Ra, R-a) first described by Aloisio and Francisco is important, and a serious omission from our simulations and discussion. In general complex formation sequesters HO_2 and so reduces our sensitivity to (R1), particularly at the lowest temperatures (where we do nonetheless observe some evidence for (R1)). Note however that even using the larger of the two published $K_a(T)$ values for this non-reactive complex (Hermans et al. 2005) the impact upon our results at 228 K is small.

The referee appears to suggest that the calculations of Aloisio and Francisco, and of Hermans et al. both underestimate K_a, and lead us to overestimate the sensitivity of our experiments to (R1). A factor of 10 error in K_a for the non-reactive acetone complex appears necessary to account for the lack of experimental evidence for (R1) observed at 228 K.

Note that in a poster at the International Symposium on Gas Kinetics in Leuven (2010) Grieman et al. presented data that appeared to confirm the calculated values of K_a derived by Aloisio et al. Thus the published calculations on K_a and unpublished experimental data suggest that we retain sufficient sensitivity to (R1).

Nonetheless, in the revised manuscript we will discuss both the impact of the published data for (Ra) on our results, and define which values of K_a would be needed to bring experimental observations into line with the calculations of Hermans et al.

As the terminal O is quasi-free,
this complex should still react with NO, to yield an OH that is more weakly H-bonded
to the carbonyl-O (see Aloisio and Francisco, 2000) and thus easily released. On the
other hand, reaction of the complex with another acetone to form the _-OH-peroxy is
not expected to contribute, as it is both energetically (by 41 kJ mol-1) and entropically
strongly disfavored compared to (R1). Besides thermal redissociation, the complex can
thermally convert, about 20 times slower, to the _-OH-peroxy, which brings the effective k1
somewhat above the low-P limit.

Likely product formation (OH) suggests that we are blind to (Ra) in these experiments (scenario 2), though they do reduce sensitivity to (R1). Slow conversion of the complex to the OH-peroxy (product of (R1)) does little to mitigate the loss in sensitivity to (R1) as the experimental timescale was too short.

More interesting perhaps is reaction of the complex to form anything other than OH (see scenario 2.1 above).

The rate of approach to the equilibrium can be approximated as kcapt x [acetone] x _scZLJ[M]/(kred(Eav) + _scZLJ[M]) (given that the term for the thermal redissociation is sizably smaller, at least at 207 K and 25 Torr). This gives an equilibration time constant of roughly 1000   s (with a large uncertainty) for the 207 K, 25 Torr, 7.5x10(14) cm-3 acetone experiments, such that at [NO] = 1.5x10(14) cm-3 much of the HO2 will already have reacted before the complex attains equilibrium.

Agree, whilst a large proportion of HO_2 is complexed (Ra) in equilibrium at 207 K, simulations show that the approach to equilibrium is too slow to remove our sensitivity to (R1).

At 228 K, 85 Torr and 1.7x10(15) cm-3 acetone however, where also the thermal redissociation term becomes important, the time constant is nearer 50 s, such that HO2 complexation is quasi-immediate. It should be stressed however that the Kcompl estimates above may be off by a factor of 10, given the _4 kJ mol-1 uncertainty on the complex stability, as stated for most relative energies in the Hermans et al. 2005 paper. Items 3 and 4 above can explain the strong apparent disagreement between the k-1 and K1 data derived in this manuscript and the predictions of Hermans et al. For instance, at 207 K, 25 Torr: a same effective k1/(1 + k-1/k2[NO]) rate as concluded to in the paper is obtained with k-1 negligible and k1 = 1.6x10(–12) cm3 s-1 (i.e. 0.27 times the k1,1 prediction of Hermans et al. 2005); and at 228 K, 85 Torr: likewise, with k-1 negligible and k1 _ 1x10(–12) cm3 s–1 (i.e. 0.33 x k1,1) but with 80-90% of the HO2 quickly complexed.

The approach to equilibrium is indeed faster at 228 K. However, the published calculations of Aloisio et al. and of Hermans et al. both indicate that even with our largest $[CH_3C(O)CH_3]$ of 1.7×10^{15} molecule cm^{-3} only a small proportion (< 20 %) of HO_2 is complexed at 228 K.
In the revised manuscript we will discuss both the impact of the published data for (Ra) on our results (scenario 3), and attempt to quantify how much larger values of K_a would be needed to bring experimental observations into line with the calculations of Hermans et al. (scenario 3.1).

5. According to the authors' interpretation of the observed [OH] behavior in Fig. 2, with a large k-1 of 30000 s-1 at T = 228 K, the second term in the denominator of the apparent rate for HO2 removal by acetone, k1[acetone]/(1 + k-1/k2[NO]) (see sub 1., above), would be much larger than 1, such that the apparent rate would simplify to K1k2[acetone][NO], and thus show the same dependence on [NO] as the rate k8[NO] of the competing HO2 + NO → OH + NO2 reaction. As a result, the competition between HO2 removal by acetone and by NO to yield OH would be independent of [NO]. If on the other hand k-1 is negligible at these T as predicted by Hermans et al., the apparent rate of HO2 removal by NO is independent of [NO], very different from the linear [NO]-dependence of the competing HO2 + NO reaction. This might have been easily checked by the authors. However, the tell-tale dependence of the competition at issue on [NO] was not investigated, all experiments at given T having having been conducted at a single [NO].

Experimental conditions were chosen both to allow detection of OH (we are not equipped to detect HO_2 directly) and to optimise the range of sensitivity to the title reaction. This was achieved by working at sufficiently large [NO] to compete with k_{-1}. There is, as the referees have made clear, plenty of scope for more experimental studies of HO_2 / $CH_3C(O)CH_3$ / NO chemistry.

6. In the light of the above, the section on atmospheric modelling in the manuscript appears rather premature.

We feel that modelling of the reaction in the atmosphere is appropriate at this stage. Even if different interpretations of the data on k_1 and K_1 need be considered, at least these different scenarios allow the reader to get a feeling for how important (R1) may be. Furthermore, the model runs considered different scenerios, eg. no (R1), K_1 from Hermans et al., and K_1 from this work.

Technical and minor Comments	
Page 16755, line 24: this should be : k-1 = 3x10(–12) cm3 molecule-1 s-1 (minus sign in exponent).	Will be amended in the revised manuscript (error was typographical – not in simulation code).
Table 3: the fast OH + HO2 reaction is missing as a (minor) OH sink.	OH + HO_2 now included in new simulations, though its affect is negligible (< 2 % in [OH] after 1 ms), considerably smaller than uncertainties from non-reactive complexes, or even the rates of established chemical reactions eg. OH +

		NO.
Table 3: A minus sign is missing in the exponent of 10 of the second term.		No need to amend our word doc - error was only in online version.
Table 3: OCH2C(O)CH3y decomposes promptly into CH3CO + HCHO instead of reacting with O2 (Orlando et al., 2000).		Was amended for recent simulations, though the impact was negligible (< 1 % in simulated [OH]).
Table 3: The expression given for k(CH3 + O2) would result at the experimental pressures in values well above the high-P limit.		Parameters for the falloff and high pressure limit (F_c = 0.27 and k_∞ = 1.8×10^{-12} $(T/300)^{1.1}$ cm^3 $molecule^{-1}$ s^{-1}) were missing from the table (not the simulation) – now included.
Table 3: The reaction of CH3CO + O2 generates about 30% OH at 207 K and 25 Torr, and about 8% at 228 K and 85 Torr.		Scheme amended to include CH_3CO + O_2 → OH, however exact yields are a matter of dispute. From recent work in this laboratory, yields of not more than 17 and 4 % are appropriate for N_2 bath gas at T < 298 K. This makes a barely discernable change to simulated OH profiles (< 1 % in [OH] after 1 ms), since little CH_3CO is produced in these experiments.
Table 3: Equilibrium formation of the _68 kJ mol-1 stable HOOOOH tetroxide from HO2 + HO2 (see Denis et al., J. Phys. Chem. A, 2009, 113, 499) is missing, but is only minor at the fairly low experimental [HO2] of this work, though quite important at the much higher [HO2] in another recent study.		The self-reaction of HO_2 was included in the simulations, though it is a negligibly slow process give the experimental conditions of small [HO_2] and large [NO]. Any impact of changing the self-reaction product from H_2O_2 to HOOOOH will be smaller than even the uncertainties in rate of reaction with NO, or of complexing with abundant CH_3OH and $CH_3C(O)CH_3$.
Page 16761, line 24: twice "in line with (the) theoretical predictions".		No need to amend our word doc - error was only in online version.
From Anonymous Referee #2		
This paper describes a laboratory study of the HO2 + acetone reaction at low temperatures. The results from this study are used as input to an atmospheric model to evaluate the significance of this chemistry with regards to acetone loss and acetic acid production. This is a rather difficult reaction to study directly and the authors have used an indirect method to extract kinetic data using modeling of experimentally measured OH profiles. The subject of this paper is definitely suitable for publication in ACP, however, I have an issue with the clarity of the paper in its present form and the thoroughness of the data analysis / interpretation.		
The description of the data analysis and determination of the rate constants and equilibrium constant in the text is difficult to follow. The data analysis requires fitting of OH temporal profiles using an extensive reaction mechanism (provided in a table), but the sensitivity of the obtained k1 and Keq values to the model parameters is not clearly established.		
There is a near linear dependence for value of K_1 reported on value for k_2 (RO_2 + NO) used. Other rate coefficients are of considerably less importance since we are always comparing OH profiles with $CH_3C(O)CH_3$ present to those at [$CH_3C(O)CH_3$] = 0. We shall clarify this point in the revised manuscript for ACP.		
The kinetic results are given in Table 2, but the reader pretty much has to take these values on faith. Another complication to the clarity of the text is the interwoven discussion of the kinetic parameters reported from previous theoretical studies. I would much prefer to know		

what the experimental data "says" independent of the theoretical calculations. The experimental results should then be compared with the theoretical predictions. If the experimental data can't be interpreted independently of the theoretical calculations that should be made more clear in the text. In the present form, I get an impression that the kinetic data for this reaction is still not well determined, i.e., I do not get a clear answer to the title of the manuscript. A few comments and typos:

The experimental data shows that a reaction between HO_2 and $CH_3C(O)CH_3$ is efficient at 207 K, $k_1 > 1.5 \times10^{-12}$ cm^3 molecule^{-1} s^{-1} and not at higher *T*. We opined that the only reasonable physical interpretation of these observations was a reaction (R1,R-1) of the type reported by Hermans, with stabilisation and efficient trapping of RO_2 (R2) at 207 K and not at 228 K and above. There are other explanations for the observations (see above), though all are related to earlier theoretical work. The experiment was of course designed to test the theoretical predictions of Hermans et al.

The atmospheric model calculations presented are reasonable, but a clearer definition of the experimental data is needed before these calculations are meaningful. Figure 5 does not really provide much useful information related to the present study. It is useful to show the model sensitivity but a comparison to field measurements of CH3C(O)OH with the model calculations is almost meaningless until better quality measurements become available.

We will present clearer explanation of the origins, values and uncertainties in K_1 for ACP (see above). The model provides a global estimation of acetic acid production via (R1), which is independent of the quality of any field data.

Page 16748, line 8: "provide evidence" should be "provide indirect evidence" ?		Amended.
Page 16748, line 12: "larger" should be "greater"		Amended.
Page 16749, line 4: provide units for E in the given Arrhenius expression, it would be better yet to just use E/R values throughout.		Amended.
Page 16750, lines 5-10: It is not clear or true that the agreement of theoretical calculations for other reaction systems should give you confidence in the Hermans et al. (2004) calculations. The reason for giving the text following these statements is also not clearly stated.		Whilst referee 1 (J. Peeters) disagrees (see above), we are happy remove any reference to gaining confidence from study of analogous systems.
Page 16751, line 13: Referring to an interference filter is rather vague, what are the optical properties?		FWHM 10 nm centred at 309 nm - details will be provided for ACP.
The discussion of the data in figures 1 and 2 given on pages 16754 and 16755 is vague and unclear. For example, on page 16755 the phrase "were in roughly inverse" is given, but then the results are referred to as "robust".		Agreed. We have deleted "roughly", which was a crude way of indicating that the data was not noise free.
Page 16755, lines 6 and 24: exponent should be "-12"		Amended.
Figure 2, caption: is the k-1 value of 30000 s-1 right? The numbers in Table 2 are not in line with such a large value.		Yes, the value is correct. Not sure what the referee means by "in line". The k_1 values in Table 2 are lower limits, so using $k_{-1} = k_1 / K_1$ a lower limit k_{-1}(228 K) = 0.1e-12 / 0.6e-16 = 1700 may be derived, consistent with $k_{-1} = 30000$ s^{-1} reported in Figure 2.

Figure 4: narrow down the range on the x-axis to reduce the amount of empty white space.		Good idea.
Table 3: The text font is too small.		Amended.
From Anonymous Referee #3		
The paper describes a laboratory study of the reaction between acetone and HO2 and a modeling study assessing the contribution of this reaction to acetone degradation in the upper troposphere. The experimental studies monitor HO2 indirectly detecting the OH product of the HO2+NO reaction. Given the large discrepancy between two recent theoretical studies of this reaction this study represents a reasonable attempt to resolve the discrepancies between the prior work. These experiments are not easy to perform at the lowest temperatures that are reported here. The difficulty here is that, in the absence of the ability to directly monitor HO2, the authors are attempting to model a poorly constrained system and they acknowledge this. They have chosen to fix the rate of the adduct + NO reaction by analogy with another peroxy reaction and use the forward addition rate from Hermans et al. to model the data. The results clearly seem to show evidence for reaction between HO2 and acetone at the lowest temperature of the experiments but the attempts to quantify the results are, in my view, rather more problematic.		
I don't think it is reasonable to arbitrarily fix two out of three rate coefficients and then report "measured" equilibrium constants. Having spent a limited time running simulations of the chemistry, I find that these simulations are very sensitive to the value of the adduct+NO reaction and yet the authors assign an uncertainty of _ 50% to this reaction although it has never been measured.		
Agreed, there is a near linear dependence for value of K_1 reported on value for k_2 (RO$_2$ + NO) used. It is difficult to assess the uncertainty in k_2, but many similar reaction rates coalesce to around the proposed 1.5×10^{-11} cm^3 molecule^{-1} s^{-1} at around 200 K. There are many rate constants unavailable at the low temperatures studied here, though they are of considerably less importance since we are always comparing OH profiles with CH$_3$C(O)CH$_3$ present to those at [CH$_3$C(O)CH$_3$] = 0. We shall clarify this point in a revised manuscript for ACP.		
It also appears that a little more could have been done to constrain some of these rate coefficients. The authors state that In all experiments, a large excess of [NO]>1*1014 molecule cm 3 was available to irreversibly trap (R2) the product peroxy radical, and prevent re-dissociation (R 1) to products. However if their estimate of R2 is correct the trapping rate coefficient at 207K would be _(1.5e-11*1.5e14)_ 2250 s-1. This is the same as their estimated dissociation rate so all the adduct molecules would not have been scavenged. It would have been informative to examine the pressure dependence of the OH temporal profiles at higher NO concentrations. If in fact the adduct was being completely scavenged then a pressure dependence in the adduct formation rate might be discernable.		
The excess [NO] = 1.5×10^{14} molecule cm^{-3} would prevent redissociation (R-1) if theoretical calculations were correct of such a back reactions rate of a few persecond at 207 K. One of the main conclusions of this work is that we are unable to prevent (R-1) even with the large [NO] indicating that the theoretical calculations from Hermans and Cours are in error. We will endeavour to clarify this issue in a redraft for ACP. There certainly are more experiments that could be done on HO$_2$ – CH$_3$C(O)CH$_3$ chemistry. We were primarily concerned with the atmospheric importance or otherwise of (R1), ie. whether the calculated k_1 and K_1 from Hermans were realistic.		
Overall I think this work merits publication. It certainly resolves the very large discrepancies in the calculated rate coefficients reported in the recent theoretical studies and suggests that the actual rate coefficient is much closer to the value calculated by Hermans et al. It also		

appears to show that that the equilibrium constant calculated by Hermans et al. is not consistent with the experimental data. I think the authors underestimate the uncertainty in their equilibrium constants but it is difficult to see how this uncertainty could be large enough to encompass this difference. This is critical in assessing the atmospheric implications since it changes the reaction from an important acetone sink to one that is of no significance. I think that inclusion of the temporal profiles in the supplementary material would be extremely useful. It is very difficult to assess a paper like this without repeating the numerical simulations and access to the all the temporal profiles would be a great help.

As we indicated in the preamble, there are other interpretations that could be applied to our experimental observations (scenarios 1-3), so yes, the uncertainties are much greater than indicated in the manuscript. We will be happy to share all raw data upon request.

From G. Tyndall (Referee)		

This study describes lab experiments designed to investigate the interaction of HO_2 radicals with acetone at low temperatures. It also includes a brief modeling section to investigate the possible effects of the reaction in the atmosphere.
The study is somewhat indirect, since it involves the conversion of HO2 radicals to OH, and detection of OH by LIF. However, the effects on the HO2 profiles shown in the
figure are consistent with a reaction, particularly at low temperatures. Overall, I am surprised that the addition reaction of HO2 with acetone appears to be so fast, but it does agree with the predictions of the paper by Hermans et al. (J. Phys. Chem. A,
2005) The study is careful, and within the uncertainties of the conversion technique and chemical modeling required to quantify the results, robust. It can be published with
some changes.

Experimental: The authors should consider the effects of methanol on the reaction scheme. A quick look at the paper of Christensen (J. Phys. Chem. A, 2006) suggests that about 20% of the HO2 should be complexed at 207 K. Could this affect the kinetics of the acetone reaction, e.g., if only uncomplexed HO2 were to react? How does the estimated rate constant for dissociation of the methanol complex compare with that for the acetone adduct or the NO reactions?
It would be useful to give the pressure(s) in the text here.

Agreed, extrapolation of the Christensen results reveals that around 20 % of HO_2 at 207 K is complexed (Rb) to CH_3OH. Our primary diagnostic is the change in OH profile upon addition of $CH_3C(O)CH_3$ to the system. Inclusion of the HO_2-CH_3OH chemistry enhances simulated OH by up to 10 % with $CH_3C(O)CH_3$ present, more than the 2 % change simulated with $[CH_3C(O)CH_3] = 0$. This slightly reduces our sensitivity to K_1 at 207 K. More important for the findings of this paper is that only $\approx$ 4 % of HO_2 should be complexed to CH_3OH at 228 K, with consequently negligible impact on our sensitivity to k_1 and K_1 where theory (Hermans) predicts a strong interaction and we observe none.

Also, in either the table or text, please give the lowest non-zero acetone concentration (zero is not particularly useful).	Agreed. The table will be amended to show lowest non-zero values.
Page 16757, line 17. "recation" should be "reaction"	Amended.
Modeling: The description of the models could be a little clearer. Which ones had the acetone reaction included?	S1 was the published reference mechanism, SR1 an update for other recent RO_2 chemistry, SR2 the full suite including (R1), (R-1). We will clarify this in any ACP submission.
Page 16760, line 5. Should be "AN additional route"	Amended.
ESM P3. "oxyde" should be "oxide"	Will be amended for ACP.

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