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Interactive comment on “Atmospheric organic-phase photo-sensitized epoxidation of alkenes by α -dicarbonyls” by G. Yu and F. N. Keutsch

Anonymous Referee #2

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The manuscript reports the well-known epoxide formation of alkenes in organic solvents in the presence of biacetyl and air. This reaction has been characterized by organic chemists (Shimizu and Bartlett in 1976), but is a new concept in atmospheric chemistry. The problem is of general atmospheric interest and may provide an explanation to laboratory studies showing the formation of organosulphate formation through an epoxide channel. However, the work has flaws that must be carefully addressed before the article can be accepted in Atmospheric Chemistry and Physics. A strong weakness of the article is the use of chloroform and benzene as solvents. The importance of the targeted organic species in the solvents used for atmospheric chemistry appears irrelevant to this reviewer. The very low Henry's constant of the species in-

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volved indicate that they partition strongly into the gas phase and will not dissolve in atmospheric liquids. Therefore, the vast majority of biacetyl, α -pinene, isoprene, MVK, etc, will be processed in the gas phase (in contrast to the assertion in pages 15117 and 15125).

If the authors would like to consider chemical reactions occurring in the liquid phase, they cannot avoid studying the system in water. The new experiments to be included in this work will have to be compared to those obtained in chloroform and benzene. Several examples in the literature should also be included in the discussion of the new results, for example, the aqueous phase processing of isoprene and alpha-dicarbonyls will need to be related (Y. Liu, A. Monod, T. Tritscher, A. P. Praplan, P. F. DeCarlo, B. Temime-Roussel, E. Quivet, N. Marchand, J. Dommen, and U. Baltensperger, *Atmospheric Chemistry and Physics*, 2012, 12, 5879; and B. Ervens and R. Volkamer, *Atmospheric Chemistry and Physics*, 2010, 10, 8219). Furthermore, the experimental method utilized resulted in unacceptable concentration changes over the course of the experiment, as indicated in p. 15118 by the excessive loss of solution by evaporation (up to 30%). The control performed (p. 15119) does not support the claim of negligible evaporations losses. The results (Table S2) indicate a rate limiting step controlled by the concentration of biacetyl and the irradiation power, and consider biacetyl as a catalysts (with negligible photolysis) whose concentration remains constant, but indicate a deviation from linearity due to solvent evaporation. All this issues need to be considered and reliable experiments with small volume changes (less than 5%) should be reported in the updated version of the manuscript.

Additional measurements are needed to quantify biacetyl using an alternative analytical method. It is unacceptable to avoid quantifying biacetyl. Acetic and peroxyacetic acids should be expected by irradiating biacetyl in water and air (Faust, B. C., K. Powell, C. J. Rao and C. Anastasio, 1997, *Atmospheric Environment* 31, 497). The discussion should consider that biacetyl is a hydrophilic alpha-dicarbonyl compounds that has been found in fogs, clouds, rain, and mists at concentrations up to tens of micromolar

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(Munger J. W., Collett Jr J., Daube Jr B. and Hoffmann M. R., 1990, Atmospheric Environment, 24B, 185; Munger J. W., Jacob D. J., Daube B. C., Horowitz L. W., Keene W. C. and Heikes B. G., 1995, J. geophys. Res. 100, 9325; and Collett Jr. J. L., Daube Jr. B. C., Gunz D. and Hoffmann M. R., 1990, Atmospheric Environment 24A, 1741). It appears that biacetyl, as indicated in Table S2 (experiment 4), could be actually a reactant instead of a catalyst. Although attempts to compare the reactivity of the species studied are made, they are completely unsupported because the manuscript does not report any quantum yield.

In conclusion, new experiments in organic solvents with small volume changes (less than 5%), experiments in water, the quantification of biacetyl by alternative techniques, a deeper discussion of other reactions pathways and intermediates that alpha-dicarbonyls produce in gas and liquid phases, and the crucial measurement of quantum yields, are needed. The major revision requested will strongly support the statement that organic aerosol in the atmosphere could serve as the solvent for epoxidation reactions or reject it. Once the previous issues have been addressed, the manuscript should be reconsidered for publication in Atmospheric Chemistry and Physics.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 15115, 2012.

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