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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Isoprene, sulphoxy radical-anions and acidity" *by* K. J. Rudziński et al.

K. J. Rudziński et al.

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The authors thank Referee Magda Claeys for her review, which helped to improve the paper.

RC: *General comments:*
This study shows that isoprene is able to react with sulphoxy radicals, giving rise to novel oxygenated isoprene derivatives, which could serve as precursors for organosulphates that have recently been reported in several laboratory and field studies. As discussed in the manuscript, it is still not clear how organosulphates are formed since direct esterification of alcohols does not seem to be kinetically feasible. The proposed reaction with sulphoxy radicals could indeed play a role in the formation of organosulphates in aqueous systems. In this respect, I would like to draw attention to a recent

study (Galloway et al., ACPD 8, 20799-20838, 2008), which demonstrated that sulphuric acid alone was not sufficient to generate the sulphate adduct of glyoxal but that irradiation (likely responsible for the formation of reactive sulphate radical anions) was also required.

I have found this an interesting study which provides novel insights into the complex chemistry of reactive sulphate species and their potential in the formation of organosulphates.

AR: The paper by Galloway et al., (2008) was published on the same day as our. Galloway et al. (2008) showed that formation of glyoxal sulphate on ammonium sulphate aerosol in chamber experiments required irradiation. They suggested the reaction was acid-catalysed by organic acids produced in parallel reactions. However, we agreed with the Referee that radical chemistry could be more likely involved, so we added this reference and a sentence on **P. 20871 - l. 27**:

"Reactions of glyoxal on ammonium sulphate aerosol produced glyoxal sulphate only upon irradiation (Galloway et al., 2008), which likely could initiate the formation of sulphate radical-anions."

RC: *Specific comments:*
P. 20870 - l. 10, 11, 12: I suggest to provide nominal m/z values, since the accuracy of the low mass resolution measurements is probably about 1 unit.

AR: We agreed and corrected the m/z values throughout the paper.

RC: *P. 20870 - l. 13: I would write: "... by electrospray ionisation mass spectrometric analysis".*

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AR: We agreed, and also added a note on possibility of structural isomers of the products. The sentence on **P.2870-l. 8-12** is now:

"Formation of sulphite and sulphate derivatives of isoprene - sulphurous acid mono-(2-methyl-4-oxo-but-2-10 enyl) ester (m/z=163), sulphurous acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester (m/z=165), sulphuric acid mono-(2-methyl-4-oxo-but-2-enyl) ester (m/z=179), sulphuric acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester (m/z=181), and possible structural isomers of these species - was indicated by electrospray ionization mass spectrometric analysis of post-reaction mixtures."

RC: *P. 20871 - l. 2: something is missing in this sentence; do the authors perhaps mean "... in the gas-phase as well as in heterogeneous and multiphase processes."?*

AR: We feel the sentence is correct, as we enumerated the gas-phase processes, heterogeneous processes and multiphase processes.

RC: *P. 20871 - l. 17: I suggest to provide the following references after ".... of some of them.": Surratt et al., 2007a,b; 2008. Please note that the Surratt et al. 2008 reference only recently became available. Ref.: Surratt, J. D., Gómez-González, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, J. Phys. Chem. A, 112, 8345-8378, 2008.*

AR: We added the references on **P. 20871 - l. 17**. The whole sentence is now:

"In summary, numerous experiments in simulation chambers, unseeded or seeded with ammonium sulphate particles, showed isoprene induced formation of aerosol that contained such compounds as methyltetrols, C_5 alkene triols, 2-methylglyceric acid, gly-

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oxal, methylglyoxal, acetals and hemiacetals, oragnosulphates and organonitrates, as well as oligomers of some of these (Surratt et al., 2007a,b, 2008). ”

RC: *P. 20873 - l. 9: I also suggest to mention here that the spectra were obtained in the negative ion mode: "Post-reaction solutions were analysed off-line and in the negative ion mode using....".*

AR: We agreed. The sentence on **P. 20873 - l. 9-11** is now:

“Post-reaction solutions were analysed off-line, and in negative ion mode using an API 365 triple quadrupole mass spectrometer with electrospray ionization from Applied Biosystems.”

RC: *P. 20875 - l. 25, 26, 27 and p. 20876 - l. 1: same comment as above about nominal m/z values. Furthermore, as an organic mass spectrometrist I would be more precise here and write: "Electrospray ionisation mass spectra of post-reaction solutions contained peaks of deprotonated molecules that could be attributed ...."*

AR: We agreed, and also expanded Sect. 3.2 to include the possible structural isomers (in: Authors Response to Anonymous Referee 1). The sentence on **P. 20875 - l. 23-27** and **p. 2076 - l. 1** is now:

“Electrospray ionization mass spectra of post-reaction solutions contained peaks of deprotonated molecules that could be attributed to products of isoprene transformation initiated by sulphite and sulphate radicals (Fig. 6), such as sulphurous acid mono-(-2-methyl-4-oxo-but-2-enyl) ester (m/z=163), sulphurous acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester (m/z=165), sulphuric acid mono-(2-methyl-4-oxo-but-2-enyl) ester (m/z=179), sulphuric acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester (m/z=181).”

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RC: *P. 20876 - l. 5: same comment as above about references: Surratt et al., 2007a; 2008.*

AR: The references on **P. 20876 - l. 5-6** are now:

"(Gómez González et al., 2007; Surratt et al., 2007a; 2008)"

RC: *P. 20894 - Fig. 6: also here I suggest to provide nominal m/z values. In addition, I suggest to be more precise in the legend about the type of mass spectra: "... appeared in negative ion electrospray ionisation mass spectra of post-reaction solutions."*

AR: We corrected Figure 6 accordingly. The caption is now:

"Fig. 6. Peaks corresponding to products of isoprene transformation coupled with auto-oxidation of S^{IV} appeared in negative ion electrospray ionisation mass spectra of post-reaction solutions."

RC: *Technical corrections:*
P. 20870 - l. 3: over a broad range
P. 20870 - l. 13: The experimental results
P. 20870 - l. 21: the distribution
P. 20871 - l. 15: methyltetrols
P. 20871 - l. 16: organosulphates
P. 20871 - l. 21: Surratt
P. 20871 - l. 25: Surratt
P. 20871 - l. 25: a recent experimental
P. 20872 - l. 18: to obtain the desired
P. 20872 - l. 20: a small amount of
P. 20873 - l. 10: electrospray ionisation

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P. 20874 - l. 23: the dimensionless
P. 20875 - l. 4: a different manner
P. 20875 - l. 21: a broad peak
P. 20876 - l. 5: Surratt
P. 20877 - l. 14: oxidation
P. 20878 - l. 25: Alkyl radicals
P. 20879 - l. 9: the respective reaction
P. 20880 - l. 19: kinetic experiments
P. 20882 - l. 27: the title of the reference should be written in lower case
P. 20882 - l. 14: Gelencsér
P. 20897 - legend Fig. 9: constants

AR: We made the technical corrections accordingly, even though we feel that 'The experimental results8230;' is equivalent to 'The results of experiments8230;'.

AR: The following references were added to the list:

P. 2082 - l. 30

"Galloway, M. M., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Flagan, R. C., Seinfeld, J. H. and Keutsch, F. N.: Glyoxal uptake on ammonium seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions, Atmos. Chem. Phys. Discuss., 8, 20799-20838, 2008, http://www.atmos-chem-phys-discuss.net/8/20799/2008/."

P. 20884 - l.23

"Surratt, J. D., Gómez-González, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, J. Phys. Chem. A, 112, 8345-8378, 2008."

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 20869, 2008.

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