

Interactive comment on “Isoprene, sulphydroxy radical-anions and acidity” by K. J. Rudziński et al.

K. J. Rudziński et al.

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The authors thank Anonymous Referee #1 for the review, which helped to improve the paper.

RC: *Detailed Review:*

For purposes of this review, the summary description in the abstract is adequate.

Does the paper address relevant scientific questions within the scope of ACP?

The paper is relevant based on the authors consideration of scientific issues in the introduction.

Does the paper present novel concepts, ideas, tools, or data?

The ideas and methods have already been presented in prior publications from the S11458

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authors. The paper expands on the conditions for the observed phenomena. The data are both new and relevant.

Are substantial conclusions reached?

The conclusions are valuable for understanding the possible formation of organic sulfates in the atmosphere. The major issue with respect to applying the work to the atmospheric chemistry of isoprene is whether the mass transfer of isoprene is sufficiently high to permit the reactions and products described in the text to be realized in atmospheric aerosol. This consideration should be included in the Conclusion Section

AR: Paragraph on **P. 20881, L.05-13**, in the Conclusions Section, was rewritten as follows:

“Reactions of isoprene with sulphony radical-anions have a few potential implications for atmospheric chemistry and atmosphere-biosphere interactions. They are another possible source of new organosulphur components of atmospheric aerosols and waters, which add to heterogeneous sources postulated recently. They can also slow down the formation of sulphuric acid and sulphate ions in atmospheric waters, and consequently reduce the formation of acidity and inorganic sulphate aerosol. Probably, reactions of isoprene with sulphony radical-anions can also influence the distribution of reactive sulphur and oxygen species inside isoprene-emitting organisms (plants, animals and humans) and on their surfaces.

Realisation of reactions of isoprene with sulphony radical-anions in real atmospheric systems has to be evaluated quantitatively by further experimental and modelling study. The preferred systems are characterised by high availability of isoprene and S^{IV} species (sulphur dioxide), either emitted locally or transported from remote areas. Good examples are rainforests, urban areas with high emissions of vehicle exhausts, sea-coastal regions, sea-atmosphere interface and surfaces of isoprene-emitting plants. The laboratory work should focus on the uptake of isoprene by aque-

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ous solutions, which is limited by low solubility of isoprene in water on one hand, but enhanced by aqueous reactions of isoprene and microphysical redistribution of reactants on the other hand. Products of reactions of isoprene with sulphy radical-anions should be searched for in field samples of atmospheric aerosols and waters.”

RC: *Are the scientific methods and assumptions valid and clearly outlined?*

Yes, but improvements can be made. The description of the mass spectroscopic analysis (p.20873, L.09) is inadequate and needs to be expanded. Moreover, the authors need to provide better justification for the identifications reported in Fig. 6. Clearly, these are tentatively identified compounds and not discovered as described in the text (p.20876, L.02).

AR: The sentence on p. 20873, L.09-L.11 was rewritten, using also the advice of Referee Magda Claeys:

“Post-reaction solutions were analysed off-line, and in negative ion mode, using an API 365 triple quadrupole mass spectrometer with electrospray ionisation from Applied Biosystems. The samples were taken immediately after each experiment, using a gas-tight syringe to prevent the access of air, and diluted with methanol before injection to the MS apparatus.”

AR: Discussion of Figure 6 was improved in expanded Sect. 3.2 (below). The word ‘discovered’ was changed to ‘tentatively identified’.

RC: *Are the results sufficient to support the interpretations and conclusions?*

Yes, but this could have been done more effectively. Section 3 entitled Results and discussion is essentially a section on results only. The Discussion itself starts with Section 4, currently titled Chemical mechanism and simulation of experiments. Certain aspects of the Section 3 and 4 are unclear and should be rewritten. For example,

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Section 3.2 is highly abbreviated and should be expanded considerable, especially with the interpretation of the UV spectra in Figure 5 and the MS in Figure 6. (...)

AR: Section 3.2 was expanded, and now includes the interpretation of the UV spectra in fig. 5, and the MS spectra in Fig. 6. The revised version is:

“ 3.2 Transformation of isoprene

The analysis of UV spectra of reacting solutions showed that in all experiments isoprene decayed proportionally to the decay of sulphite. The ratio of these conversions ranged from 0.21 to 0.40, and to 1.21, the latter value being rather uncertain as calculated from conversions lower than 1 % (Table 1). In neutral and slightly acidic solutions, we saw weak light absorption by non-sulphate reaction products, with a broad peak at 240 nm (Fig. 5). The peak was positioned at longer wavelengths than the 225 nm peak of isoprene (Rudzinski,2004), and close to the 239 nm peak of the unsaturated aldehyde 3-methylbut-2-enal, $(\text{CH}_3)_2\text{C}=\text{CH}-\text{CHO}$, calculated using the increment method (Hesse et al., 1997): 207 nm for the base structure $-\text{C}=\text{C}-\text{CHO}$ in methanol + 24 nm for two CH_3 groups + 8 nm for water replacing methanol as a solvent. Two structural isomers of this aldehyde had calculated peaks at positions a little more distant: $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)-\text{CHO}$ at 237 nm, and $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)\text{O}$ at 233 nm. All three carbonyls are similar in structure to possible products of isoprene transformation in our experiments, which additionally contain sulphate or sulphite substituents. We cautiously suggest that spectra in Fig. 5 indicate these products, because the influence of sulphate or sulphite groups on the UV absorption above 200 nm is likely negligible. Unfortunately, other possible products of isoprene transformation, which contain hydroxyl groups instead of carbonyl oxygens, would not absorb the UV light between 200 and 300 nm, and, if present, were invisible to our absorbance measurements.

Electrospray ionisation mass spectra of post-reaction solutions contained peaks of deprotonated molecules that could be attributed to products of isoprene transforma-

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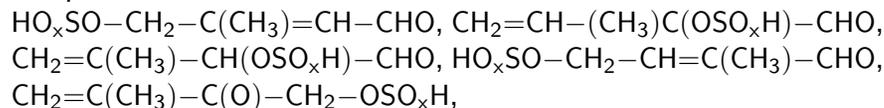
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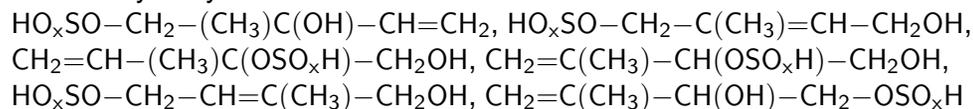
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tion initiated by sulphite and sulphate radical-anions (Fig. 6), such as sulphurous acid mono-(-2-methyl-4-oxo-but-2-enyl) ester ($m/z=163$), sulphurous acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester ($m/z=165$), sulphuric acid mono-(2-methyl-4-oxo-but-2-enyl) ester ($m/z=179$), and sulphuric acid mono-(4-hydroxy-2-methyl-but-2-enyl) ester ($m/z=181$). Test analyses excluded the possibility of analytical artefacts, showing that the peaks did not appear in spectra of freshly prepared solutions containing isoprene and sodium sulphate or isoprene and sodium sulphite. The compounds shown in Fig. 6 are examples of several structural isomers, which could be produced in our experiments and attributed to the observed MS peaks. A sulphonyl radical can add to double bonds in isoprene at four different positions. Consequently, further reactions can produce five -oxo- isomers



and six -hydroxy- isomers



for each type of sulphonyl radical involved ($x = 2$ for sulphite radical, and $x = 3$ for sulphate radical). Identification of individual isomers was not possible in this work, and would require higher yields of the products, and commercial or synthesised standards that were not available. However, three of the -oxo- compounds were also indicated by the UV spectra discussed in the previous subsection.

Whatever their exact structure is, the tentatively identified compounds have double carbon-carbon bonds that can react further, for instance with radical species. Saturated organosulphates produced in such reactions would be similar to sulphate esters of methylglyceric acid and 2-methyltetrols that had been detected in field samples of atmospheric aerosols (Gómez González et al., 2007; Surrat et al., 2007a, 2008). ”

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RC: (...) *The discussion of Section 4.1 (and Figure 7) could easily be eliminated given its minor importance to the subject matter. At worst, combine Sections 4.1 and 4.2 with the major focus on the material in 4.2. Section 4.4 is presently terse and should be expanded particularly the last two paragraphs. I would suggest a single mechanism be presented with consecutively numbered rate constants. Right now it is almost impossible to correlate the numerical values for the rate constants in Table 2 with where they are found in the three mechanisms presented. (...)*

AR: We would like to keep the chemical mechanism divided into three separate modules, both in sections and in figures, because we feel it is more transparent than one combined mechanism. A modular mechanism would be easily refined, modified or extended in future studies. For instance, the mechanism of auto-oxidation of Mn^{II} ions in presence of S^{IV} (Sect. 4.1) is necessary to allow reproduction of our model simulations, but in other studies or applications can be replaced with other sources of Mn^{III} .

We left out the numbering of reactions in Figs 7-9 to simplify the reaction schemes. Instead, we used the specifically named rate constants, which associated with respective chemical reactions better than the consecutively numbered constants. We included these reasons in the sentence on P. 20876, L. 20-22. To reduce the difficulties in cross-referencing the rate constants between figures, text sections and Table 2, we rearranged Table 2 and included explicit guide-lines in it. We also added a missing k_{2s5} constant. New Table 2 was placed at the end of this Interactive Comment. Now, the sentence on **P. 20876. L. 20-22**) is:

“The individual reactions in the schemes were identified by specific symbols of the rate constants rather than by consecutive numbers, to simplify the presentation and provide better mnemonic association.”

AR: We expanded second subsection and two last subsections in Sect 4.4:

(**P. 20879, L. 20 - P. 20880, L. 02**) was replaced by
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“The results of simulation were compared to matching experiments in figures arranged according to the initial values of pH of reacting mixtures. Time traces of reactant concentrations were shown in Figs. 10 and 11, while changes of pH of reacting solutions were shown in Fig. 12. Generally, time traces of S^{IV} and oxygen concentrations were reproduced with good accuracy at all acidities. Consumption of isoprene was simulated quite accurately in acidic solutions, but was overestimated in basic and neutral solutions. The simulation was still accurate qualitatively, reproducing the right shapes of isoprene time traces from all experiments. The quantitative disagreement was explained by the deficiency of the mechanism used, which treated the primary nonradical products of isoprene degradation as nonreactive. Each of these products contained a double C-C bond, which could react with radicals in solutions to influence the overall inhibiting or accelerating action. In the present mechanism, ‘all the work’ had to be done by isoprene, which consequently appeared to decay faster than in the experiments. The effect was more pronounced in basic and neutral solutions, because conversion of isoprene was higher than in acidic solutions. In addition, the mechanism would probably gain still more quantitative flexibility, if included all primary nonradical products of isoprene transformation (Sect. 3.2), not the four necessary representatives (Sect. 4.3).”

(P. 20880, L. 10 - 17) was replaced by

“The acidity of reacting mixtures was reproduced quite well, with the exception of experiments that started at $pH_0 = 8.3$ and included isoprene, in which the experimental acidity decreased, while the simulated acidity slightly increased. This disagreement could be explained by the ability of functional groups in isoprene derivatives to bind free protons from solutions, which had not been included in the present mechanism. In acidic and basic solutions, the effect was masked by high yields of free protons released upon oxidation of HSO_3^- ions to SO_4^{2-} . It became visible in basic solutions, just because the initial reservoir of dissociable protons was smaller by orders of magnitude, while the extremely low initial concentration of free protons ($\sim 5 \times 10^{-9}$ M) was

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very sensitive to even small shifts in the protonation-deprotonation balance of species whose concentration was higher by three or four orders of magnitude. Thus, the prediction of hydrogen ion concentration in basic solutions should improve, if the protonation and deprotonation reactions of isoprene esters are added to the mechanism.

In summary, the results of simulation showed that the proposed mechanism of isoprene transformation during autoxidation of S^{IV} was a reasonable approximation of the real-life chemistry in our experiments. The experimental and simulated data agreed very well qualitatively, and well quantitatively. The shapes of the concentration time traces, and the stoichiometry of transformation were reproduced accurately. The qualitative performance of the mechanism reflected its adequate structure. The quantitative performance can still improve within this structure, for instance if a better set of reaction rate constants is used. The working set of rate constants used for the presented simulation contained many constants, whose values were guessed by fitting, and should be replaced by values determined in future experiments. Further improvement is expected, if the mechanism is extended by adding the reactions indicated in this section. Despite the present limitations, the mechanism is ready for application in future studies.”

RC: (...) *Section 5 (Conclusions) should have a better focus on the atmospheric implications of the work especially the reported formation of reported organic sulfates in the atmosphere. How is the present work able to clarify these observations, if at all?*

AR: This comment was addressed above, within the answer to the first comment on Conclusions.

RC: *Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? The experimental methods section could be strengthened with respect to the mass spec measurements and the oxygen measurement.*

AR: Description of the mass spec measurements was improved above, when answering the comment on scientific methods and assumptions. For the oxygen measurement, two sentences were added on **P. 20873, L. 04**, and the next sentence was slightly modified:

“The oxygen electrode was calibrated before each experiment against the electronic zero and the local atmospheric pressure, using a built-in circuitry. The concentration of dissolved oxygen was read directly from the pH-meter, in ppmO₂. Voltage signals from both pH-meters were recorded every 0.1 s, and converted to pH and oxygen concentration in mol dm⁻³, using a computer system equipped with a M6281 data acquisition card and a LabView application, both from National Instruments.”

RC: *Do the authors give proper credit to related work and clearly indicate their own new/original contribution?*

Yes. However, the authors should have included the following reference: Limbeck et al., Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles, Geophys. Res. Lett., 30, doi:10.1029/2003GL017738, 2003.

AR: We reviewed the work by Limbeck et al. (2003) in (Rudzinski, 2006; 2008). They considered the influence of H₂SO₄ on SOA yields indirectly. We added this reference on **P. 20871 L. 21**:

“In particular, sulphuric acid and sulphur dioxide increased the yields of aerosol (Jang et al., 2002; Limbeck et al., 2003; Surratt et al., 2007b).”

RC: *Does the title clearly reflect the contents of the paper?*

The title is a bit too terse and should include the type of phenomena being examined.

AR: We changed the title:

“Reactions of isoprene and sulphy radical-anions - a possible source of atmospheric organosulphates and organosulphites”

RC: *Does the abstract provide a concise and complete summary?*

The abstract should include more detail on the differences for the auto-oxidation reaction in neutral and base solutions. This is one case where the model apparently did a poor job in compound predictions as noted in the text.

AR: Expanded Sect. 4.4 (above) explains more clearly the quantitative deviation of model-simulated isoprene from the experiments in basic and neutral solutions, and shows the qualitative prediction was good. The opposite trends in pH in experiment at initial pH = 8.3, in presence of isoprene are shown quantitatively minor. We added a following sentence to the Abstract, (**P. 20870 L. 19**):

“In basic and neutral solutions, the model overestimated the consumption of isoprene, probably because reactions of primary sulphite and sulphate derivatives of isoprene with sulphy radicals were not included. ”

RC: *Is the overall presentation well structured and clear?*

The structural changes and the issue of clarity are considered above.

AR: We addressed the respective comments above.

RC: *Is the language fluent and precise?*

The language needs work. Here are some suggested changes.

- (p.20870, L.02 and throughout the text) replace autooxidation with auto-oxidation
- (p.20871, L.09) replace tetraols with tetraols
- (p.20871, L.13) replace in a nutshell with in summary; In a nutshell is jargon.
- (p.20874, L.07) replace exemplary with sample; inappropriate usage

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- (p.20875, L.09) replace *got* with *were*
- (p.20876, L.02) replace *discovered* with *tentatively identified*; one would need a calibration standard.
- (p.20876, L.09) delete *protection*
- (p.20886, footnote) replace *are inaccurate* with *have increased uncertainty*

AR: We made all the suggested changes, but one (- (p.20876, L.09) delete *protection*). We just meant the environmental protection technology. Now, we made the sentence more clear:

“Auto-oxidation of S^{IV} catalysed by manganese was studied extensively in the context of both atmospheric chemistry and technology of cleaning the industrial waste gases or wastewaters.”

RC: *Are mathematical formulae, symbols, abbreviations, and units correctly defined and used?*

The rate constants should be number consecutively to make them easier to follow.

AR: Within the answer to comment to Sect. 4 (above), we explained why we would like to keep the named constants.

RC: *Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?*

For the size of the document, 12 figures seems excessive. The mechanism in Figs.7-8 should be combined into a single figure, if not all three mechanisms into a single figure. A better discussion in the text should be given for Figures 10-12.

AR: We would like to keep the mechanism divided into three parts for the reasons given above, within answers to the comments on Sect 4. Better discussion for Figures 10-12 was provided in expanded section 4.4, above.

RC: *Are the number and quality of references appropriate?
The reference list looks complete except for Limbeck et al. (2003) noted above.*

AR: The following references were added to the revised manuscript:

Hesse, M., Meier, H. and Zech, B.: Spectroscopic Methods in Organic Chemistry, Georg Thieme Verlag, Stuttgart, New York, 1997.

Limbeck, A., Kulmala, M. and Puxbaum, H.: Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles, Geophys. Res. Lett., 30, doi:10.1029/2003GL017738, 2003.

RC: *Is the amount and quality of supplementary material appropriate?
n/a*

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

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Table 2. Rate constants used for simulation of chemical mechanism shown in Figs 7-9.

Constant in Fig. 7	Value $M^{-1} s^{-1}$	Constant in Fig. 8	Value $M^{-1} s^{-1}$	Constant in Fig. 9	Value $M^{-1} s^{-1}$
k_{ass}	1.0×10^{11}	k_{ass}	1.0×10^{11}	k_{s1}^k	2.19×10^9
k_{dys}^a	6.75×10^3	k_{dys}^a	6.75×10^3	k_{s2}	1.0×10^9
k_{kfb}	6×10^6	k_{ib}	1.0×10^3	k_{s3b}	1.0×10^9
k_{kbb}	1	k_{ia}	3.0×10^1	k_{s3a}	1
k_{kfa}	6×10^6	k_{p1}^d	1.5×10^9	k_{s4b}	1.0×10^9
k_{kba}	1	k_{p21b}^e	3.25×10^6	k_{s4a}	1.0×10^9
k_{afb}	6	k_{p22b}^e	9.75×10^6	k_{s5}	$(1 \div 5) \times 10^4$
k_{abb}	1	k_{p21a}^e	2.5×10^4	k_{s6}^l	3.5×10^9
k_{afa}	$8 \div 10$	k_{p22a}^e	7.5×10^4	Analogous constants for reactions of SO_3^- radicals (not shown in figures)	
k_{aba}	1	k_{p3b}^f	1.4×10^7		
k_{dfb}	6	k_{p3a}^f	1.4×10^7		
k_{dbb}	1	k_{ox11}	3.2×10^6		
k_{dfa}	$8 \div 10$	k_{ox12}	1.2×10^2		
k_{dba}	1	k_{ox2}	1.0×10^6		
k_{o2b}	6	k_{t22}^g	1.0×10^8	k_{2s1}	1.0×10^9
k_{o2a}	$8 \div 10$	k_{cas}	1.0×10^{10}	k_{2s2}	1.0×10^9
k_{hpb}^b	0.19	k_{cdy}^a	3.98	k_{2s3b}	5.0×10^4
k_{hpa}^c	3.4×10^7	k_{fb}	7.5×10^3	k_{2s3a}	1.0×10^6
		k_{fa}	7.5×10^3	k_{2s4b}	$(1.2 \div 2.5) \times 10^4$
		k_{t1}^h	4.0×10^8	k_{2s4a}	5.0×10^4
		k_{t21}^i	1.0×10^7	k_{2s5}	1
		k_{t3}	1.0×10^6		
		k_{t4}^j	5.0×10^8		

a s^{-1} . b Drexler et al. (1992). c $M^{-2} s^{-1}$, rate = $k_{hpa}[H^+][H_2O_2][HSO_3^-]$, Drexler et al. (1991).

d Huie and Neta (1984). e Huie and Neta (1987). f Averaged in CAPRAM24.

g 5.5×10^6 Herrmann et al. (1995), $\sim 2.2 \times 10^8$ Buxton et al. (1996).

h Waygood and McElroy (1992). i 1.3×10^8 Herrmann et al. (1995), 4.8×10^7 Buxton et al. (1996).

j McElroy and Waygood (1990). k Rudzinski (2004). l 1.7×10^9 Buxton et al. (1996).

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