Atmos. Chem. Phys. Discuss., 13, C2035–C2053, 2013
www.atmos-chem-phys-discuss.net/13/C2035/2013/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Radical mechanisms of methyl vinyl ketone oligomerization through aqueous phase OH-oxidation: on the paradoxical role of dissolved molecular oxygen" *by* P. Renard et al.

P. Renard et al.

pascal.renard@etu.univ-provence.fr

Received and published: 6 May 2013

RC C740: 'Review of the manuscript', Anonymous Referee #3, 23 Mar 2013

The authors appreciate many important comments raised by Reviewer 3 which have been considered in the new version of the manuscript. The authors' answers to the questions/comments of Reviewer 3 are presented below.

General comment

Question: Overall, this work is very well done and can be publishable. However, the

introduction should be improved to meet the publication standard. The authors should clearly state the motivation of this work with more comprehensive literature review. Furthermore, the atmospheric implications of their observations should be better discussed in the revised version.

Answer: We fully agree on these general comments, and we have modified the introduction and conclusions accordingly (see answers to specific comments).

Specific comments:

Question: Introduction: first of all, the introduction gives an overall impression that oligomerization process is highly relevant to all aqueous medium, including aerosol, fog and cloud water, in the atmosphere but this is actually inappropriate. Previous studies (e.g. Tan et al., 2009, Lim et al., 2010) have shown that high precursors concentration is a critical factor to facilitate radical mechanism for the formation of oligomeric products, which may only relevant to the aerosol scenario. The authors should provide more accurate interpretation on the literature findings. Secondly, the authors attempt to use a single term "non-oxidative reaction pathways" (page 2916, line 24) to generalize the potential mechanisms of oligomerization without further interpretations. What types of "non-oxidative reaction pathways" has been suggested by Mazzoleni et al (2012) and other studies? Giving a few examples of potential mechanisms and other field/lab observations in the introduction is highly recommended. For example, Turpin and co-workers have illustrated the possibility of radicalradical oligomerization to produce high molecular weight products with aqueous-phase OH oxidation as an initiation step. This is particularly important for readers to build up their understanding on this specific research topic and the motivation of this study. Lastly, it is recommended to add the motivation of modifying the selected experimental conditions here instead of simply stating what have been done. This would definitely help to visualize the potential atmospheric implications of this work in the later part of manuscript.

Answer: We agree on this and we have modified the introduction accordingly, here is the new introduction: "Although Secondary Organic Aerosol (SOA) represents a substantial part of organic aerosol, which affects air quality, climate and human health, the understanding of its formation pathways and its properties is still limited due to the complexity of the physicochemical processes involved. It is now accepted that one of the important pathways of SOA formation occurs through aqueous phase chemistry (Hallquist et al., 2009; Carlton et al., 2009; Ervens et al., 2011). In particular, a number of studies have observed the formation of large molecular weight compounds in atmospheric aerosols (see for example Clayes et al., 2004, and 2010; Baduel et al., 2011) and in cloud/fog droplets (Herckes et al., 2002 and 2007), and the presence of HUmic-LIke Substances (HULIS) in atmospheric aerosol particles, fog and cloud water has been reviewed by Graber and Rudich (2006). Recent studies have shown that aqueous phase chemistry of glyoxal (Volkamer et al., 2007 and 2009; Ervens and Volkamer, 2010; Lim et al., 2010), methylglyoxal (Tan et al., 2012), pyruvic acid (Guzmàn et al., 2006; Tan et al., 2012) glycolaldehyde (Ortiz-Montalvo et al., 2012), methacrolein and methyl vinyl ketone (El Haddad et al., 2009; Liu et al., 2012) can produce significant amounts of SOA. In particular, Volkamer et al., (2007 and 2009) and Ervens and Volkamer, (2010) have shown that SOA production can occur via liquid phase processes of glyoxal in deliquesced particles named wet aerosol, where ambient relative humidity (RH) range from 50 to 80%. These findings give an extremely large set of conditions where organic liquid phase processes can occur, i.e. from rain drop, cloud and fog droplet to wet aerosol, for which atmospheric lifetimes (< 1 minute – days), liquid water content (LWC : 108 - 1 μg m-3), surface area (10-2 – 10-10 cm^2), particle number concentration (10-4 – 104 cm-3) and individual organic and inorganic chemical concentrations (10-2 – 106 μM) vary over orders of magnitude (Ervens and Volkamer, 2010). In their review, Lim et al. (2010) report that liquid phase reactions of glyoxal with OH radicals performed under high initial concentrations tend to be faster and form more SOA than non-radical reactions. They conclude that in clouds/fog conditions (i.e. diluted concentrations of 10-2 – 1 mM), radical reactions yield organic acids, whereas in wet aerosols (i.e. concentrated conditions of 10 mM – 10 M) they yield

large multifunctional humic-like substances, or oligomers, formed via radical-radical reactions. An oligomer is a molecule that consists of a few monomer units (from 2 to up to 30). Lim et al. (2010) and Tan et al. (2012) propose that radical-radical reactions to form oligomers are alkyl-alkyl radical additions, which always compete with O2 addition reactions. This explains why oligomer formation is observed only at high initial precursor concentrations, inducing high alkyl radical concentrations (after initial OH-oxidation of the precursor) which are required for radical-radical reactions to take place in competition with the reaction of O2. However, O2 concentrations were supposed to stay constant at saturation (i.e. Henry's law equilibrium) in these studies, as they were only measured and the beginning and at the end of the reaction. In the present study, in order to determine the atmospheric relevance of radical reactions, we explore in details the radical mechanisms and the influence of O2 concentrations on this chemistry using a slightly different precursor, i.e. methyl vinyl ketone. This compound is an α,β-unsaturated carbonyl that is water soluble, it bears a highly reactive function (i.e. carbon-carbon double bond) which is likely to play a major role on radical chemistry and oligomer formation, as it was preliminarily shown by Liu et al. (2012). The reactivity of olefin compounds has been scarcely studied in the liquid phase up to now, although a number of field measurements have observed them in atmospheric waters: unsaturated diacids were detected in rain and fog samples (7-14% of the total mass of diacids: Kawamura et al., 1993 and 1994 and Sempéré et al., 1996) and in marine aerosols (2-7% of the total mass of diacids; Fu and Kawamura, 2013). In clouds, it was observed that 1-18% of the total mass of carbonyls were unsaturated carbonyls (among which methylvinylketone) (van Pinxteren et al., 2005), and in biogenic aerosols, unsaturated polyols (C5-alkene-triols) represented 2-5% of the total mass of identified polyols (Claeys et al., 2010). Finally, using NMR spectroscopy, Decesari et al. (2000) detected that 10-35% (respectively 7-37%) of the organic chemical functions were unsaturated in fog samples (respectively aerosols) in the Po Valley. In view of these numbers, one can reasonably suppose that 2-20% of the organic matter concentration is unsaturated in atmospheric waters. Therefore, assuming total water soluble organic compounds

(WSOC) concentrations of 0.01-1 μM in rain drops, 1-100 μM in cloud droplets, 1-100 mM in fog droplets and 1-10 M in wet aerosol, one obtains a range of unsaturated organic compounds of 0.002-0.2 μM in rain drops, 0.02-20 μM in cloud droplets, 0.02-20 mM in fog droplets and 0.02-2 M in wet aerosol. The aim of the present study was to determine the radical mechanism involved in the oligomerization of MVK, and to identify the oligomers formed via this chemistry. MVK was used as a model compound for unsaturated organic compounds present in atmospheric waters, its initial concentrations were varied from 0.2 to 20 mM, thus representing the total concentrations of unsaturated organic compounds in fog droplet and wet aerosol. In order to determine the atmospheric relevance of this radical chemistry, the influence of temperature and dissolved oxygen concentrations were studied."

Question: 2. Section 3.1.1, Page 2925, line 24-25: Formation of oligomers were clearly observed based on the mass-spectrometric analysis. However, this statement implies that NMR can be used as a stand alone technique to at least qualitatively indicate the presence of oligomers in the reacting solution. It is worth to provide appropriate references to support the way to interpret the NMR spectra in this section.

Answer: Alarifi, A. and Aouak, T.: Homopolymerization of benzylmethacrylate and methylvinylketone using Ni(acac)2–methylaluminoxane catalyst system, Arabian Journal of Chemistry 2, 87– 93, 2009.

Ziaee, F., Bouhendi, H. and Ziaie, F.: NMR Study of Polyacrylamide Tacticity Synthesized by Precipitated Polymerization Method, I. Poly. J., 18 (12), 947-956, 2009.

Question: 3. Conclusions and atmospheric implications: The conclusion can be shorten because there are too many details of repeated information from the previous section. Instead, the authors should better discuss the atmospheric importance of their current observations. In particular, due to the fact that atmospheric droplets has much larger surface to-volume ratio than that of the bulk solution, oxygen molecule in the droplets likely equilibrate with the surrounding air quickly, resulting in saturation of

dissolved oxygen. This suggests that the proposed oligomerization mechanism may be significantly inhibited. The atmospheric relevance of the initial MVK concentrations (0.2, 2, and 20 mM) used in this study should be also addressed. In addition, ozone may react with the C=C bond of MVK quickly through heterogeneous processing, especially under high ozone concentration. Can the authors roughly estimated the relative importance between ozonolysis and the proposed oligomerization mechanisms on the consumption of C=C bond of MVK in the atmospherically relevant condition?

Answer: We agree on these comments and we have modified the conclusions accordingly. Here are the new conclusions, which have been renamed "atmospheric implications", and which contain a new figure (Fig. 12) and a new table (Table 3): "The proposed mechanism allowed for explaining the particular role of dissolved O2 under our experimental conditions. Each iRâĂć radical underwent competition kinetics between O2 addition (reaction R1) and oligomerization (reaction R2):

iRâĂć + O2 → LMWC kR1 (R1)

iRâĂć + n(MVK) → oligomers kR2 (R2)

Supersaturated (by a factor of 155%) initial O2 concentrations inhibited radical oligomerization by fast addition on iRâĂć resulting in the formation of LMWC (such as acetic acid and methylglyoxal), which were further OH-oxidized and formed other iRâĂć radicals. The fast O2 addition reactions resulted in a fast decrease of O2 concentrations in the vessel, faster than O2 renewal from the gas phase and from the reactivity of H2O2, and even faster than MVK consumption. At initial MVK concentrations higher than 0.2 mM, the decrease of O2 concentrations resulted in the dominance of reaction (2) after several minutes, and oligomerization started, even when O2 concentrations were still higher than Henry's law equilibrium with atmospheric O2. The paradoxical role of O2 resides in the fact that while it intensely inhibits oligomerization, it produces more iRâĂć radicals, which contribute to O2 consumption, and thus lead to oligomerization. These processes, together with the large ranges of initial concentrations investigated (60 – 656 μM of dissolved O2 and 0.2 – 20 mM of MVK concentrations) show the fundamental role that O2 likely plays in atmospheric waters. In order to scale the relative importance of reactions R1 and R2 from the laboratory to the atmospheric conditions, one has to compare the rates of R1 and R2: vR1 = kR1 $\times$ [iRâĂć] $\times$ [O2] vR2 = kR2 $\times$ [iRâĂć] $\times$ [MVK] The dominance of oligomerization over O2 addition is determined by v_R2/v_R1 =k_(R2)/k_R1 $\times$[MVK]/[O_2] . Assuming that the ratio k_R2/k_R1 does not vary from the laboratory conditions to the atmospheric ones, one can simply predict the oligomerization to occur from the [MVK] / [O2] ratio. In our experiments, the detailed study of the time profiles of O2 and MVK together with the kinetics of oligomer formation allowed us to determine that radical oligomerization dominates over O2 addition for [MVK] / [O2] ratios (in M/M) equal or higher than 32 (at 5°C) and 54 (at 25°C). In atmospheric waters, assuming that dissolved O2 concentrations are saturated (i.e. at Henry's Law equilibrium) everywhere from 0 to 5 km in altitude, and from -20 to +25°C, gives a range of 190-391 μM for [O2]. Furthermore, taking the concentrations of unsaturated organic compounds ([UNS]) in atmospheric waters as stated in the introduction, one obtains [UNS] / [O2] ratios as indicated in Fig. 12 (Ervens et al., 2012). In this figure, radical oligomerization occurs when [UNS] / [O2] ratios are equal or higher than 32 or 54. It is thus concluded that radical oligomerization will always occur in wet aerosols, and in sometimes in fogs: in most polluted fogs, where [UNS] > 6 mM. This result, added to the fact that the lifetime of wet aerosols in the atmosphere are several days, shows the extreme relevance of radical oligomerization of unsaturated organic compounds in the atmosphere. Another point of view for atmospheric implications is the fate of MVK. In general, aqueous phase OH-oxidation is known to drastically reduce WSOCs atmospheric lifetimes, compared to their gas phase reactivity (Monod et al., 2005). As it was shown in the present study, once in the liquid phase, MVK can undergo OH-oxidation. In fogs and wet aerosols, it can additionally undergo oligomerization with a first order kinetic rate constant of koligo = 7.6 ($\pm$ 0.3) x 10-4 s-1, (which is not temperature dependent between 5 and 25°C) as derived in the present work from the MVK decay during oligomerization, under all conditions (figures

5 and 9). Although MVK is weakly water soluble, its aqueous phase reactivity may impact its overall atmospheric lifetime. In Table 3, we compare MVK atmospheric lifetimes between its gas phase reactivity only (taking into account both OH-oxidation and ozonolysis) and its multiphase reactivity. The latter takes into account MVK air/water partitioning at Henry's Law equilibrium, and its liquid phase reactivity: oligomerization is considered only in fogs and aerosol media. Table 3 shows that liquid phase reactivity impacts the overall atmospheric lifetime of MVK by 2 to 13%. Compared to these numbers, the rate of heterogeneous ozonolysis of MVK on SiO2 or ïĄą-Al2O3 particles under various relative humidity (ïĄğ = 10-10 to 10-9, Shen et al., 2013) calculated for a number of 100 nm particles of 5000 particles cm-3, would deplete its atmospheric lifetime by less than 0.00006%. Thus, liquid phase photooxidation seems more efficient, but this needs to be confirmed by more studies of both bulk and heterogeneous reactivity of olefin compounds. The results obtained in Figure 12 and Table 3 show the atmospheric relevance of liquid phase reactivity of unsaturated water soluble organic compounds (even for low soluble ones like MVK), and their ability to activate radical oligomerization chemistry, which is extremely fast and is able to form macromolecules as high as 1800 Da in polluted fogs and wet aerosols. For an unsaturated compound 10 times more soluble than MVK, we anticipate that its overall atmospheric lifetime would be depleted by 13 to 79%, thus showing the need for further studies of oligomer formation from other relevant unsaturated compounds, and their mixtures under various conditions (especially inorganic content and ionic strength). Further studies are also needed to investigate the oligomer yields, their oxidizing states, and their aging (Siekmann et al., in preparation).

Fig. 12: Estimated ranges of the ratios of unsaturated dissolved organic carbon concentration to oxygen concentration (in M M-1) in atmospheric waters. The straight lines delimit the values for which radical oligomerization dominates over O2 addition, as determined by the present work (see text).

Table 3: Comparison of MVK atmospheric lifetimes between its gas phase reactivity

only and its multiphase reactivity, taking into account its air/water partitioning at Henry's Law equilibrium, its gas and liquid phase reactivity: oligomerization is considered only in fogs and aerosol media, with koligo values derived from our experimental results.

Minor comments:

Page 2918, line 19-20: Please briefly describe the method used for H2O2 detection.

Answer: We used UPLC-UV at 265nm for H2O2 detection.

Table 1: I am wondering if the dissolved oxygen concentration without H2O2 was measured. This can confirm the supersaturation of dissolved oxygen.

Answer: Dissolved oxygen concentrations were continuously monitored in the solution before, during and after H2O2 introduction. This is visible on Figure 9, where one can see that O2 was saturated prior to H2O2 introduction. Just after H2O2 introduction, dissolved O2 concentrations increased and reached a supersaturation concentration, certainly due to the following reactions: H2O2 + HOâĂć → HO2âĂć + H2O HO2âĂć + HO2âĂć → H2O2 + O2 HO2âĂć + âĂćO2- (+H+) → H2O2 + O2 Then, when MVK was introduced, dissolved O2 concentrations decreased due to addition on alkyl radicals. All this is explained in the manuscript (sections 2.2.3 and 3.3.2).

Page 2929, line 23-28: Duplicate information in this paragraph.

Answer: This paragraph was rewritten to avoid duplicate information.

Figure 9: In order to visualize the delay of oligomer formation in the case of high dissolved O2 concentration, it is recommended to add the time series profile of total signal from oligomers in Figure 9a-c.

Answer: These changes have been done in the new version of Fig. 9

Page 2933, line 11: Perhaps typos. ": : :Supplement 2: : :"

Answer: The typo concerned the reaction number (R7 instead of R2). The sentence

has been replaced the following one: this method of identification, applied to the synthetic oligomers of MVK formed from the V-50 initiator, allowed us to identify the most intense series of oligomers as the one shown in reaction 2 R7 (in Supplementary Information 2), thus showing the robustness of the method.

References

Alarifi, A. and Aouak, T.: Homopolymerization of benzylmethacrylate and methylvinylketone using Ni(acac)2–methylaluminoxane catalyst system, Arabian Journal of Chemistry 2, 87– 93, 2009.

Baduel, C., Voisin, D., Jaffrezo, J.L.: Seasonal variations of concentrations and optical properties of water soluble HULIS collected in urban environments, Atmos. Chem. Phys., doi:10.5194/acp-10-4085-2010.

Bateman, A. P., Walser, M. L., Desyaterik, Y., Laskin, J., Laskin, A., and Nizkorodov, S. A.: The Effect of Solvent on the Analysis of Secondary Organic Aerosol Using Electrospray Ionization Mass Spectrometry, Environ. Sci. Technol., 42(19), 7341-7346, doi:10.1021/es801226w, 2008.

Benson, B. B. and Krause, D.: The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere, American Society of Limnology and Oceanography Inc., Department of Physics, Amherst College, Amherst, Massachusetts, USA, 1984.

Carlton, A. G., Wiedinmyer C., and Kroll J. H.: A review of Secondary Organic Aerosol (SOA) formation from isoprene, Atmos. Chem. Phys., 9, 4987–5005, 2009.

Chen, Q., Liu, Y., Donahue, N.M., Shilling, J.E. and Martin, S.T., Particle-Phase Chemistry of Secondary Organic Material: Modeled Compared to Measured O:C and H:C Elemental Ratios Provide Constraints, Environ. Sci. Technol., doi.org/10.1021/es104398s, 45, 4763–4770, 2011.

Claeys, M., Wang, W., Ion, A.C., Kourtchev, I., Gelencsér, A. and Maenhautc, W.: Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide, Atmospheric Environment, 38, 4093–4098, 2004.

Claeys, M., Kourtchev, I., Pashynska, V., Vas, G., Vermeylen, R., Wang, W., Cafmeyer, J., Chi, X., Artaxo, P., Andreae, M. O. and Maenhaut, W.: Polar organic marker compounds in atmospheric aerosols during the LBA-SMOCC 2002 biomass burning experiment in Rondônia, Brazil: sources and source processes, time series, diel variations and size distributions, Atmos. Chem. Phys., 10, 9319–9331, 2010.

Danger, G., Orthaus-Daunay, F.R., de Marcellus, P., Modica, P., Vuitton, V., Duvernay, F., Flandinet, L., Le Sergeant d'Hendecourt, L., Thissen, and R., Chiavassa, T.: Characterization of laboratory analogs of interstellar/cometary organic residues using very high resolution mass spectrometry, Geochimica Cosmochimica (submitted).

Decesari, S., Facchini, M.C., Fuzzi, S., McFiggans, G.B., Coe, H., and Bower, K.N.: The water-soluble organic component of size-segregated aerosol, cloud water and wet depositions from Jeju Island during ACE-Asia, Atmospheric Environment 39, 211–222., 2005.

Decker, C. and Jenkins A. D.: Kinetic approach of O2 inhibition in ultraviolet- and laser-induced polymerizations, Macromolecules, 18, 1241, DOI: 10.1021/ma00148a034, 1985.

El Haddad, I., Liu, Y., Nieto-Gligorovski, L., Michaud, V., Temime-Roussel, B., Quivet, E., Marchand, N., Sellegri, K., Monod, A.: In-cloud processes of methacrolein under simulated conditions e part 2: formation of secondary organic aerosol. Atmos. Chem. Phys. 9, 5107e5117, 2009.

Ervens, B. and Volkamer, R.: Glyoxal processing by aerosol multiphase chemistry: towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles. Atmos. Chem. Phys. 10, 8219-8244, 2010.

Ervens, B., Turpin, B.J., and Weber, R.J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, Atmos. Chem. Phys., 11, 11069-11102, 2011.

Ervens, B., Wang, Y., Eagar, J., Leaitch, W. R., Macdonald, A. M., Valsaraj, K. T. and Herckes, P.: Dissolved organic carbon (DOC) and select aldehydes in cloud and fog water: the role of the aqueous phase in impacting trace gas budgets, Atmos. Chem. Phys., doi:10.5194/acpd-12-33083-2012, 2012.

Fu, P., Kawamura, K., Usukura, K. and Miura, K.: Dicarboxylic acids, ketocarboxylic acids and glyoxal in the marine aerosols collected during a round-the-world cruise, Marine Chemistry 148 (2013) 22–32, 2013.

Gibian, M. J. and Corley, R. C.: Organic radical-radical reactions. Disproportionation vs. combination, Chem. Rev., 73 (5), pp 441–464, doi:10.1021/cr60285a002, 1973.

Gilman J.B., Vaida V. Permeability of Acetic Acid through Organic Films at the Air-Aqueous Interface. J. Phys. Chem. A, 110, 7581-7587, 2006.

Graber, E. R. and Rudich, Y.: Atmospheric HULIS: How humic-like are they? A comprehensive and critical review, Atmos. Chem. Phys., 6, 729-753, doi:10.5194/acp-6-729-2006, 2006.

Guzman, M. I.; Colussi, A. J.; Hoffmann, M. R.: Photoinduced oligomerization of aqueous pyruvic acid, J. Phys. Chem. A, 110, 3619-3626; doi 10.1021/jp056097z, 2006.

Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N.M., George, C., Goldstein, A.H., Hamilton, J.F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M., Jimenez, J.L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th.F., Monod, A., Prévôt, A.S.H., Seinfeld, J.H., Surratt, J.D., Szmigielski, R., Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys. 9, 5155-5236, 2009.

Herckes, P., Lee, T., Trenary, L., Kang, G., Chang, H. and Collett Jr., J.L.: Organic matter in central California radiation fogs, Environ. Sci. Technol. 36, 4777–4782, 2002a.

Herckes, P., Hannigan, M.P., Trenary, L., Lee, T. and Collett Jr., J.L.: Organic compounds in radiation fogs in Davis (California), Atmos. Res. 64, 99–108, 2002b.

Herckes, P., Leenheer J.A. and Collett Jr., J.L.: Comprehensive Characterization of Atmospheric Organic Matter in Fresno, California Fog Water, Environ. Sci. Technol. 41, 393-399, 2007.

Herrmann, H., Hoffmann, D., Schaefer, T., Bräuer, P., and Tilgner, A.: Tropospheric aqueous phase free radical chemistry: radical sources, spectra, reaction kinetics and prediction tools, Chem. Phys. Chem. 11, 3796e3822, 2010.

Hobby, K.: Micromass MS Technologies, Floats Road, Manchester, M23 9LZ, UK, A novel method of isotope prediction applied to elemental composition analysis, Waters Corporation, 2005.

Huang, D., Zhang, X., Chen, Z.M., Zhao, Y., and Shen, X.L.: The kinetics and mechanism of an aqueous phase isoprene reaction with hydroxyl radical, Atmos. Chem. Phys. 11, 7399e7415, 2011.

Hughey, C.A., Hendrickson, C. L., Rodgers, R.P. and Marshall, A.G.: Kendrick Mass Defect Spectrum: A Compact Visual Analysis for Ultrahigh-Resolution Broadband Mass Spectra, Analytical Chemistry, 73(19), p.4676-4681, 2001.

Iraci, L.T., Baker, B.M., Tyndall, G.S., and Orlando, J.J.: Measurements of the Henry's law coefficients of 2-methyl-3-buten-2-ol, methacrolein, and methyl vinyl ketone, J. Atmos. Chem. 33, 321e330, 1999.

Kawamura, K. and Ikushima, K.: Seasonal Changes in the Distribution of Dicarboxylic Acids in the Urban Atmosphere, Environ. Sci. Technol., 27, 2227-2235, 1993.

Kawamura, K., Kasukabe, H., Barrie, L.A.: Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: one year of observations.Atmos. Environ. 30, 1709–1722, 1996a.

Kroll J. H. and Seinfeld J. H., 2008. Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. Atmospheric Environment 42 3593–3624.

Li, Y. and Schellhorn, H.E.: Rapid kinetic microassay for catalase activity, Journal of Biomolecular Techniques 18, 185–187, 2007.

Liao, H. and Seinfeld, J.H.: Global impacts of gas-phase chemistry-aerosol interactions on direct radiative forcing by anthropogenic aerosols and ozone, Journal of Geophysical Research: Atmospheres, doi: 10.1029/2005JD005907, 2005.

Lim, Y.B., Tan, Y., Perri, M.J., Seitzinger, S.P., and Turpin, B.J.: Aqueous chemistry and its role in secondary organic aerosol (SOA) formation, Atmos. Chem. Phys. 10, 10521-10539, 2010.

Liu, Y.: Etudes des impacts de la réactivité en phase aqueuse atmosphérique sur la formation et le vieillissement des Aérosols Organiques Secondaires sous conditions simulées, PhD-Thesis, Laboratoire de Chimie de l'Environnement, Aix-Marseille University (France), 2011.

Liu, Y., El Haddad, I., Scarfogliero, M., Nieto-Gligorovski, L., Temime-Roussel, B., Quivet, E., Marchand, N., Picquet-Varrault, B., and Monod, A.: In-cloud processes of methacrolein under simulated conditions - part 1: aqueous phase photooxidation. Atmos. Chem. Phys. 9, 5093-5105, 2009.

Liu, Y., Siekmann, F., Renard, P., El Zein, A., Salque, G., El Haddad, I., Temime-Roussel, B., Voisin, D., Thissen, R., and Monod, A.: Oligomer and SOA formation through aqueous phase photooxidation of methacrolein and methyl vinyl ketone, Atmos. Environ., Volume 49, pp. 123-129., doi:10.1016/j.atmosenv.2011.12.012, 2012.

Makarov, A., Denisov, E., Lange, O. and Horning, S.: Dynamic Range of Mass Accuracy in LTQ Orbitrap Hybrid Mass Spectrometer, Journal of the American Society for Mass Spectrometry, 17(7), 977-982, doi:10.1016/j.jasms.2006.03.006, 2006.

Monod, A., Poulain, L., Grubert, S., Voisin, D., and Wortham, H.: Kinetics of OH-initiated oxidation of oxygenated organic compounds in the aqueous phase: new rate constants, structure-activity relationships and atmospheric implications, Atmos. Environ., 39, 7667–7688, 2005.

Nozière B., Voisin D., Longfellow C.A., Friedli H., Henry B.E., Hanson D.R. The Uptake of Methyl Vinyl Ketone, Methacrolein, and 2-Methyl-3-butene-2-ol onto Sulfuric Acid Solutions. J. Phys. Chem. A, 110 (7), 2387-2395, 2006.

Odian G.: pp.200-205, Principles of polymerization, published by John Wiley & Sons, Inc., Hoboken, New Jersey, 2004.

Ortiz-Montalvo, D.L., Lim, Y.B., Perri, M.J., Seitzinger, S.P. and Turpin, B.J.: Volatility and Yield of Glycolaldehyde SOA Formed through Aqueous Photochemistry and Droplet Evaporation, Aerosol Science and Technology, 46:9, 1002-1014, 2012.

Orthous-Daunay, F.R. : Empreinte moléculaire des processus post-accrétionnels dans la matière organique des chondrites carbonées, PhD-Thesis, Institut de Planetelogie et d'Astrophysique, Université Joseph Fourier in Grenoble (France), 2011.

Pearce, E. M., Wright, C. E., and Bordoloi, B. K.: Laboratory Experiments in Polymer Synthesis and Characterization, Educational Modules for Materials Science and Engineering Project, Elsevier, USA, 1–22, 1982

Schuchmann, H.-P. and von Sonntag, C.: Methylperoxyl radicals: a study of the γ-radiolysis of methane in oxygenated aqueous solutions. Z. Naturforsch b 39,217–221, 1984.

Sempéré, R. and Kawamura, K.: Comparative distributions of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban atmosphere, Atmo-

spheric Environment Vol. 28, No. 3, pp. 449-59, 1994.

Shen X., Zhao Y., Chen Z., Huang D. Heterogeneous reactions of volatile organic compounds in the atmosphere. Atmospheric Environment 68, 297-314, 2013.

Tan, Y., Carlton, A. G., Seitzinger, S. P., and Turpin, B. J.: SOA from methylglyoxal in clouds and wet aerosols: Measurement and prediction of key products, Atmos. Environ., 44, 5218–5226, 2010.

Tan, Y., Lim, Y. B., Altieri, K. E., Seitzinger, S. P. and Turpin, B. J., Mechanisms leading to oligomers and SOA through aqueous photooxidation: insights from OH radical oxidation of acetic acid and methylglyoxal. Atmos. Chem. Phys., 12, 801–813, 2012.

Tilgner, A. and Herrmann, H., 2010. Radical-driven carbonyl-to-acid conversion and acid degradation in tropospheric aqueous systems studied by CAPRAM, dx.doi.org/10.1016/j. atmosenv.2010.07.050.

Vaïtilingom M., Deguillaume L., Vinatier V., Sancelme M., Amato P., Chaumerliac N., Delort A.M. Potential impact of microbial activity on the oxidant capacity and organic carbon budget in clouds. PNAS, 110, 559–564, 2013.

van Pinxteren, D., Plewka, A., Hofmann, D., Müller, K., Kramberger, H., Svrcina, B., Bächmann, K., Jaeschke, W., Mertes, S., Collett Jr., J.L., Herrmann, H.: Schmücke hill cap cloud and valley stations aerosol characterisation during FEBUKO (II): organic compounds. Atmos. Environ. 39, 4305-4320, 2005.

Volkamer, R., SanMartini, F., Molina, L. T., Salcedo, D., Jimenez, J., and Molina, M. J.: A missing sink for gas-phase glyoxal in Mexiko City: formation of secondary organic aerosol, Geophys. Res. Lett., 34, L19807, doi:10.1029/2007GL030752, 2007.

Volkamer, R., Ziemann, P. J., and Molina, M. J.: Secondary Organic Aerosol Formation from Acetylene (C2H2): seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase, Atmos. Chem. Phys., 9, 1907-1928, doi:10.5194/acp-9-1907-2009, 2009.

von Sonntag, C. and Schuchmann, H.-P.: Peroxyl radicals in aqueous solution, In: Alfassi, Z.B. (Ed.), Peroxyl Radicals, Wiley, Chichester, pp. 173–234, 1997.

Wang, W.-F., Schuchmann, M. N., Schuchmann, H.-P., and Sonntag, C. v.: The importance of mesomerism in the termination of a-carboxymethyl radicals from aqueous malonic and acetic acids, Chemistry - A European Journal, 7, 791-795, 2001.

Yadav, L. D. S.: Organic Spectroscopy, Kluwer Academic, Secaucus, NJ, U.S.A., pp. 7-51, 2012.

Zhang, X., Chen, Z.M., and Zhao, Y.: Laboratory simulation for the aqueous OH-oxidation of methyl vinyl ketone and methacrolein: significance to the in-cloud SOA production, Atmos. Chem. Phys. 10, 9551-9561, 2010.

Ziaee, F., Bouhendi, H. and Ziaie, F.: NMR Study of Polyacrylamide Tacticity Synthesized by Precipitated Polymerization Method, I. Poly. J., 18 (12), 947-956, 2009.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 2913, 2013.

Fig. 12: Estimated ranges of the ratios of unsaturated dissolved organic carbon concentration to oxygen concentration (in $M\ M^{-1}$) in atmospheric waters. The straight lines delimit the values for which radical oligomerization dominates over O_2 addition, as determined by the present work (see text).

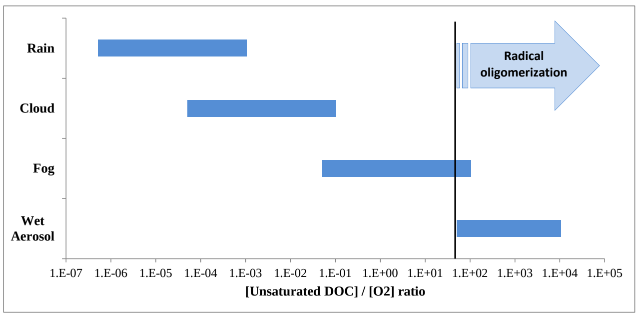

Fig. 1. Figure 12

Table 3: Comparison of MVK atmospheric lifetimes between its gas phase reactivity only and its multiphase reactivity, taking into account its air/water partitioning at Henry's Law equilibrium, its gas and liquid phase reactivity: oligomerization is considered only in fogs and aerosol media, with k_{oligo} values derived from our experimental results.

	gas	cloud		fog		aerosol
OH concentration	10^{6} molec cm^{-3}	10^{-13} M		10^{-12} M		10^{-11} M
O_3 concentration	$1,23.10^{12}$ molec cm^{-3} (50 ppbV)	-		-		-
Radical oligomerization reactions	No	No		Yes [a]		Yes [a]
Henry's Law constant ($M\ atm^{-1}$)	-	41[b]		41 [b]		7100 [c]
LWC ($g\ m^{-3}$)	-	5	1	0.4	0.1	2.5×10^{-5}
Atmospheric lifetimes (h) $_{at\ 298\ K}$	12	10.4	11.6	10.4	11.5	11.8
% impact of liquid phase reactivity	-	-13%	-3%	-13%	-4%	-2%

[a] $k_{oligo} = 8 \times 10^{-4}\ s^{-1}$; [b] Iraci et al., 1999; [c] Nozière et al., 2006.

Fig. 2. Table 3