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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric chemistry of carboxylic acids: microbial implication versus photochemistry" *by* M. Vaïtilingom et al.

Anonymous Referee #2

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This manuscript presents an experimental determination of the rates of biodegradation and of photodegradation of organic acids in simulated and real cloud water. The results show that biodegradation is an important sink for these compounds in cloud droplets, comparable or, under certain conditions, more important than photodegradation.

The scientific objectives of this work are relevant and the experiments generally well conducted. Based on the results presented, the conclusions seem sound and the overall message of the paper is clear. However, the quality of the presentation is not sufficient for publication. Some information is missing on the photodegradation experiments to demonstrate the validity of the results. The presentation of previous works and of the literature is not satisfactory either: important literature is missing while some citations are irrelevant or out-of-place. The structure of the paper also needs to be im-

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proved for clarity. All these improvements need to be made before publication.

Detailed comments:

1) Presentation of the literature

The literature cited, in particular in the introduction, is surprising as many important papers are not cited while others are irrelevant or out-of-place.

- the first part of the introduction and related literature (li. 7-10) discusses secondary organic aerosols, the relevance of which to the present paper is dubious. If the argument here is that the cloud processing of organic compounds can produce SOA, just say it like this and give specific references supporting this. For instance, Blando & Turpin, Atmos. Environ., 34, 1623, 2000, and more recent papers from the same group.

- In the literature of the role of cloud chemistry (li. 11-13 of the introduction), some groundbreaking literature is missing, such as Lelieveld and Crutzen, Nature, 343, 227, 1990; Lelieveld and Crutzen, J. Atmos. Chem., 12, 229, 1991; Herrmann et al., Chemosphere, 38, 1223, 1999; Monod and Carlier, Atmos. Environ., 33, 4431, 1999.

- the references supporting the fact that carboxylic acids dominate the organic compounds in cloud droplets need to be reinforced (the text gives only one, Marioni et al., 2004). This is a surprising statement, in particular in the abstract, and needs to be double checked.

- quoting review articles focusing on aerosols, not cloud droplets (Goldstein and Galbally, 2007; Hallquist et al., 2009) to support the fact that organic acids are aqueous-phase products (li. 20-21) is completely out-of-place. On the other hand, many more studies have identified organic acids in aqueous-phase reactions in laboratory, which should be cited there.

2) Previous works and experimental information

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- some results from previous works, which are used as the basis and/or justification for the present work, are insufficiently presented. For instance, in the statement li. 26-27 of p. 4883 “the aqueous phase of clouds also contain insoluble biological material. . .” it is not clear if it has been proven that biological material was present in all the droplets of a cloud, or in only some of them (for instance in 1 out of 10 or 1 out of 1000 droplets). Also, has this material been found in cloud water from many different regions ? Most of the references quoted seem to refer to the Puy de Dome station. This information is directly relevant to estimate the importance of the processes studied here in the real atmosphere.

Another point that needs clarification is that, since similar experiments have already been made by the same group (Vaitiligom et al., 2010), what is exactly the new information targeted by the present study ? If previous works already showed that biodegradation can compete with chemical degradation, why this new study ?

- Some important information on the photodegradation experiments are missing. This information might be provided in the previous papers from the same group, but the present manuscript needs to give enough information to support the results and conclusions. For instance, there is no information on how the rate constants of photodegradation are measured (section 2.6). A vague reference to a “linear regression” is made in section 2.6 but a linear regression of what ? This probably refers to the first-order decay of the organic compounds, but no detail is given. Also, the title “Calculation of the degradation rates” is confusing. The whole point of this work was to measure these rates experimentally, not to calculate them, wasn’t it ?

In addition to the information on the determination of the rates (in fact, rate constants), a figure illustrating the principle of the measurement should be provided. For instance, a figure showing the decay of the organic concentration. This would at the same time clearly show how these measurements were performed and justify that the decays were first order and that Equations (1)-(3) can indeed apply. The other reviewer and external comments have addressed the question of the concentrations of H2O2 and OH in these

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experiments. Showing the decay of organics would indicate if H2O2 was in excess and OH concentration was constant during these experiments. If neither the concentrations of organics or of OH were constant, I do not understand how the rate constants were measured, therefore it is important to clearly explain these measurements.

- for the results, Tables 2 and 3 must absolutely be presented in a similar manner (i.e “marine” vs “continental” in row or in column in both tables. . .) so that the rates in these tables can be compared directly. Although the text is not clear about the typical concentration of cells in cloud droplets, section 2.2 suggests that it is of the order of 108 cell L-1 (and this is an information that should be given more clearly). Thus, multiplying all the rate constants in Table 2 by this figure gives directly rate constants to compare with those in Table 3. This is a simple and clear way to present the results, that could be used in the abstract and conclusion.

3) Structure/presentation of the paper

- the abstract needs to be shorten and more synthetic, i.e. focus on the main results. Right now, the abstract is difficult to read because too much detail is given on the experimental conditions and the rate constants obtained, and the main conclusion is lost. Also, it would be more informative (and clearer) in the abstract to give a range of values for the rate constants of biodegradation in mol s-1 (thus assuming an average concentration of cell) to compare directly with the photodegradation constants. Chemical sources and sinks for compounds are usually given in as rates (s-1) or rate constants (mol s-1), and the results in this paper should be presented in a way that can be directly compared to these.

- the structure of the manuscript towards the end is quite confusing and needs to be shorten and clarified. Right after section 3.2 “photodegradation”, it would be more logical to present current section 3.4, which also presents experiments, and keep current section 3.3 for the discussion, since it only presents a discussion of the concentration of OH given by different models.

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Having section 3.3 as a first part of the discussion (section 4) would also allow to regroup some information, which is right now redundant between both, in particular the paragraph from li. 23 p. 4895 to li. 25 p. 4896, also discussing the concentration of OH reported by different models.

- once the discussion on the relevant concentrations of OH is made and the rate constants for bio- and photodegradation compared, the last part of the discussion should focus on the main results and conclusions of the paper. Describing the strategy of the work in detail (li.3 p. 4895 and following) or lengthy discussions of various cloud events are out of place here. In general, the conclusion should be much more synthetic, i.e. shorten and the main points made more clearly.

Once all these changes made, the manuscript should be considerably easier to follow.

Small comment: - li 4 of abstract: “catalyzer” should be “catalyst”

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 4881, 2011.