

Review on:

Enhanced photodegradation of dimethoxybenzene isomers in/on ice compared to in aqueous solution

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The article assesses experimentally the rates of disappearance of three variously substituted dimethoxybenzenes in aqueous solutions, frozen in a freezer, liquid nitrogen, and deposited from the vapor phase onto the surfaces of ice and snow. 1,2- and 1,3 – DMOBs do not react in either a liquid or a frozen aqueous solution because they do not absorb applied light; 1,4-DMOB, by contrast, absorbs and reacts. Importantly, the vapor-deposited compounds react in cases of all the isomers. Independently of the experiments, the absorption spectra of the compounds on the ice surface are calculated. The topic is appropriate for atmospheric chemistry and physics and features substantial novelty, as these compounds have not been photolyzed in/on ice to date. The research embodies an extension of the authors' previous papers on different compound (Hullar et al., 2020). I appreciate the fair effort of the authors to contribute towards expanding the knowledge of the photochemical fate of compounds in the frozen state, which is indispensable in describing the fate of the compounds in the cryosphere. The article presents a substantial amount of data. Regrettably, I have certain reservations concerning the quality of the data, correctness of the performed actinometry, and proper mathematical treatment of the kinetics and interpretation. Moreover, I have identified a number of nomenclature issues that are inconsistent with their common use. I suggest that these issues be addressed by the authors prior to the acceptance of the manuscript.

Conceptual problems:

1. Equation 1 treats the heterogenous mixture as homogeneous. There is abundant literature to support the heterogeneity of the compounds in the frozen sample (Bartels-Rausch et al., 2014) (Heger et al., 2007). Generally, at least three environments are available: a) surface; b) veins and pools; c) crystals in which the QY (quantum yields) can vary. Regarding the formation of the crystals, the freeze-concentration effect and solubility should be discussed. The photochemistry in the crystals can yield photoproducts different from those in solutions. The authors, however, discuss only the concentrations of the reactants. Could they comment on the photoproducts as well? The heterogeneity of the reacting mixture can result in a non-monoexponential disappearance of the reactants; therefore, the adherence of the experimental data to the supposed monomexponential decay should be shown.
2. The authors should expose that the increased disappearance rates for the VD (vapor deposited) compounds are not due to merely the lower concentration in the irradiated samples. For this purpose, the absolute concentrations of the compounds should be provided.
3. To calculate the QY, the knowledge of the absorbed number of photons is required; I do not assume this is reliably estimable from the current data (for the heterogenous samples and with a large uncertainty of the current disappearance rate constants and absorbance). Thus, I feel that most of the discussion is markedly speculative and should be announce in this way.

4. The absorption spectra were simulated for ice surface. How can the authors ensure that they are correct? Does the applied method reproduce solvatochromic shifts in a solution for some known compounds? Can the simulation be done for an FCS (freeze concentrated solution)? Concerning further issues associated with the simulation of the spectra: I suspect the formation of crystals on the ice surface by vapor deposition (Ondrušková et al., 2018) and frozen (amorphous) solution in the veins by LN freezing. (Ondrušková et al., 2020) Therefore, I think that the simulation should attempt to distinguish the FCS, ice-air interfaces and crystals of the compounds. In other words, even though the simulation could correctly predict interaction of compounds with the ice surface, that does not need to be the main species in the prepared sample. The authors are invited to address this issue.
5. As the employed actinometer, *o*-nitrobenzaldehyde, absorbs and photoreacts up to 366 nm and 404 nm (Leighton et al., 1934), the correction for the DMOBs is very imprecise and possibly inapplicable. I propose that the absorption spectra of the studied compound be plotted together with *o*-nitrobenzaldehyde to show the spectral overlap (or the lack of it). Monochromatic light (filtered low pressure mercury lamp) would be preferable for the actinometry (besides the polar sun experiments).
6. The aggregation of compounds in nature is reported in ice, e.g., (Mulvaney et al., 1988). I agree that both the separated and the aggregated compound can photoreact. It would be worth discussing under which natural circumstance the compounds do and do not aggregate. As a matter of fact, I cannot find in the article a proof that the compounds are not aggregated under the current experimental conditions.

Suggestions:

1. The mechanisms, photoproducts, and rate constants for the photochemically induced reactions of DMOBs should be reviewed to allow a mechanistical explanation of the proposed changes.
2. The introduction and results suffer from permanent referencing to previous research of the authors, to such an extent that the present manuscript is not comprehensible without simultaneous reading of the articles published in the past. In this context, I strongly recommend that a full description of the sample preparation be included in particular. For a reader, it is generally inconvenient to have to refer to the authors' previous publications to learn how each sample was prepared.

Formal and nomenclature problems:

1. **QLL**: the term is not used properly, e.g., lines 44-45, Table 1, and throughout. QLL (synonyms disordered interface, surface melting...) forms on the surfaces of pure water ice. At a moment of inserting impurities in, the layer is not QLL but a brine layer – that should be recognized in the manuscript. In the manuscript, the QLL is sometimes also confused to specify the ice-air surface. QLL forms in any surface of ice crystals, not just on the ice-air interface but also at grain-boundaries (Wettlaufer et al., 2006); this use of the term is also in (Barret et al., 2011) for example. A quasi brine layer was introduced to describe the brine at subeutectic temperatures (Cho et al., 2002). I strongly recommend that these distinct terms be kept in separate uses to avoid further confusion.
2. I would like to ask the authors to adhere to the correct nomenclature regarding the disappearance of the chemical compounds. Firstly, the “**photochemical reaction rate**”

constant" (line 122) is not defined. A photochemical reaction starts with the absorption of light and is followed by some relaxations like intersystem crossing, internal conversion, fluorescence, and reactions from the excited state – the individual processes can be characterized by rate constants and quantum yields. The rate constants are typically fast ($k=10^7-10^3 \text{ s}^{-1}$), measured by techniques applying pulsed lasers (Givens et al., 2008; Klán et al., 2009). Such rate constants are, however, not measured here. I feel strong urge to create the nomenclature that avoids any possible confusion between these rate constants and the apparent rates of compounds disappearance. Thus, statements such as that on line 106 "... a faster reaction rate,..." (and many others) should be avoided, as the reaction rate implicitly describes the rate of some reaction step or overall reaction, which is not being determined here. In reality, the reaction rates can be altered by the freezing; thus, statements like that on line 106 can be interpreted in a other way than that intended by the authors. What the authors are describing (eq. 1) should be, in my view, called the **apparent rate of compound disappearance**. The adjective "apparent" or an applicable synonym would clearly indicate that no rate of chemical reaction or of an elementary step is discussed. The measured apparent rate of compound disappearance depends of the photon flux, distance from the lamp, filters applied, ... whereas the rate of the chemical reaction does not.

3. **Molar absorptivity** is not correct term. I suppose the author means "molar absorption coefficient" and should use this term throughout.
(<https://goldbook.iupac.org/terms/view/M03972>)
4. The rate constant for the light absorption is a term without a physical meaning in a discussed context. Light is absorbed instantly (in order of femtoseconds or less).

Data collection problems

Importantly, the presented data mostly report insufficient sampling and reproducibility, together with inadequate irradiation times or a too weak light source. For example, Figure S2a shows an increasing concentration of the compound in the dark experiment. How is this explained? I suggest statistical testing if the concentration after the preset time (at the end of the irradiation) significantly differs from that at the beginning. Besides the data in Figures S6f, S7a-c, 10, 11b-c, I do not think the statistical testing would reveal the influence of irradiation (or time in general). In the negative case, the data should not be used in further analysis, and the experimental design should be improved.

Example Figure1c.: The conversion in 1,500 min ranges from ca 0.5 to 2 %. Such a small conversion with this large spread does not allow reliable estimate of the apparent rate constant. If the uncertainty of the slope were calculated, this fact would be apparent.

The data in Figure 1 are presented in such a manner that there does not seem to be any difference in the rate of photodegradation in first three preparation approaches. As a matter of fact, a closer look at Figures S1-12 indicates that under the performed experimental conditions the difference cannot have been detected. This fact must be emphasized in the manuscript. The post hoc Tukey-Kramer test does not reveal the issue. The performed analysis (discussed in the text) corroborates the inconclusive experiments, as most of the outputs are not significant and are highly scattered. This makes the appropriateness of publishing these data questionable.

The negative apparent rates of photochemical degradation should not be reported and should warn the authors about their experimental design.

At the same time, considering my own experience in the preparation of frozen samples, I know that these samples tend to produce heterogenous outputs; therefore, I really value the authors' work. Only, I press on not to conclude from the data the outputs that they do not offer. Still, the difference in the vapor-deposited samples is apparent and worth publishing, on the condition that the absolute concentrations are shown.

Data treatment problems

A major question rests in whether the observed rate of the compound disappearance, under steady irradiation, will follow a monoexponential decay. To respond to this issue, there are a number of reasons that indicate why it will not: For example, if the ice creates a non-homogeneous environment where compounds undergo degradation with unequal quantum yields or if the photoproduct would absorb. Importantly, the authors should show the data and analyze their deviations (residuals) from the monoexponential decay (without the logarithmic linearization).

Linearization of the kinetics was required before the availability of computers. Today, there is no basis for the method. Moreover, the exponential fit provides proper weighting of each of the points, whereas linearized one does not. Fitting the exponential decay curve and plotting the data in this way would allow the authors to determine more easily if the fit makes sense and if the sample was exposed to the light long enough.

Sample preparation:

Importantly, the absolute concentrations of the compounds in the VD (vapor deposited) samples should be given.

Further, the exact temperature of the vapor deposition may play a role, too: The fluorescence spectroscopy of naphthalene showed that an amorphous layer forms at 77 K, whereas microcrystals emerge at 253 K. (Ondrušková et al., 2018) The monolayer was never detected. I suspect the microcrystals formation under the here reported "laboratory freezer" experimental temperature.

Particular comments:

44-46 The sentence is misleading for above mentioned reasons.

96 The cited publication often observes the bathochromic shifts in both frozen and VD samples. Comparison of these differences may be important for the current study.

98-102

Importantly, there is a literature report on 100 nm shift in the absorbance upon freezing. (Heger et al., 2007) As a matter of fact, the aggregation on the ice surfaces in the experiments does always need to be a disadvantage: the same processes are to be expected to occur in the nature during the metamorphosis processes.

124 "normalizing each to the measured photon flux.." I am worried, that the photon flux is measured at the different wavelengths, thus is not much applicable.

168 How was the homogenous irradiation guaranteed? Were the samples rotated? Please, provide some detail, how much variance can be the photon flux and how much variability comes from the sampling and chemical analysis.

204 Why should the dark loss follow first order disappearance? And does it?

312 “normalized rate constant is statistically indistinguishable from zero” This is important. This is saying that the data are too noisy to draw any conclusion from. I think the authors should stress this fact. Still, the possible conclusion is that VD samples react more readily than the aqueous or frozen.

375 The experimental spectra of molar absorption coefficients reported in SI are valuable contributions. There will be even more valuable, if provided with standard errors of means, which should be available to the authors. Please, provide them.

488-490 The absorption properties in FCS is possibly more altered than on the ice surface due to more intensive interactions in that environment.

491 A reference for the QY is missing.

539 ...in snow or ice” Could the authors elaborate what changes do they expect on these two environments and why?

608 Gaussian curve fitting. Before the fit, data should be converted to scale with energy. (Antonov, 1997) More than two transitions are apparent – as discussed in the text (611) however only one curve is plotted in the Figure S19.

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