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Comment on acp-2021-553

Cornelius Zetzsch (Referee)

Referee comment on "Investigations into the gas-phase photolysis and OH radical kinetics of nitrocatechols: implications of intramolecular interactions on their atmospheric behaviour" by Claudiu Roman et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-553-RC1>, 2021

This manuscript represents a considerable progress in the structure – activity relations for reactions of OH with monocyclic aromatic compounds. It deals with a highly relevant class of aromatics for atmospheric chemistry, the hydroxy-nitrated phenols, and I recommend its publication in ACP.

The electron delivering lone-pair substituents (hydroxyl) interact with an electron withdrawing substituent (nitro) via the highly conductive aromatic p system and (even more) directly via H bonds to the nitro group. The H bond appears to increase the electron withdrawing capability of the nitro group enormously, resulting in a lower rate constant of electrophilic addition. A most striking example is the extremely low reactivity of 4-methyl-5-nitrocatechol, where the effect of the electron-delivering methyl group is completely overrun by this interaction (even increasing the effect) and leads to an even lower reactivity than 4-nitrocatechol. Similar effects of the nitro group have been observed by the authors for the nitrophenols and can be expected for anilines and thiophenes (and possibly heterocyclic and polycyclic and multifunctional compounds), which occur as metabolites and can deliver electrons via the p system and an H atom to form an H bond to the vicinal nitro group.

The same interaction shows up convincingly in the gas-phase IR spectra, where the the H bond between the vicinal OH groups appears as broadened peak around 3100 wavenumbers for catechol and shifts to almost 3400 wavenumbers for 4-methyl-5-nitrocatechol. I would like to suggest that these most interesting IR spectra are added to the title: "Investigations on the gas-phase photolysis, IR spectra and OH radical kinetics of nitrocatechols: Implications of intramolecular interactions on their atmospheric behavior" and that the outcome should appear in the abstract (see below) and be discussed in a little more detail.

The determination of the rate constants with two different reference compounds and the

photolysis constants for two wavelengths (an illustration of these data is missing) has excellent quality, and the authors might wish to add the values of the wall reactions of figs. 1-4 to the figure captions (or to table 2). The abstract should include the photolysis of all studied compounds by mentioning the photolytic lifetimes and the upper limits of 28 h for the atmosphere instead of the photolysis constants. It is not clear from the heading of the right column in table 2 that the lifetime refers to the atmosphere (do not mention the 365 nm here but explain that this has been calculated on the basis of NO₂ photolysis in the chamber). Are UV spectra of the compounds available to give an estimate of quantum yields at the wavelengths of 254 and 365 nm?

Have any products from the reaction with OH or of photolysis been observed and identified from their IR spectra?

Considering fig. 5, additional figures of the gas-phase IR spectra of the nitrophenols of table 3 (and possibly the triols) are desirable to demonstrate if the H bonds show up and obey similar systematics (and if available). Surprisingly, you do not discuss the H bond and its shift to higher wavenumbers in the nitrated catechols, where you might indicate the shifts by arrows from the relevant peaks of 4MCAT via 5M3NCAT to 4M5NCAT and from CAT via 3NCAT to 4NCAT.

It would be nice to add a table with the wavenumbers (and widths) of the bands assigned to OH and O...H bonds and to discuss these and their shifts, the removal of the doublet and shape in terms of bond strength and loss of symmetry. The position of the OH stretching vibration is also slightly shifted and may be taken as a measure of the bond energy and portion of the abstraction channel. This may add value to the mesomeric/electromeric effects discussed in figure 6. In fact, the description of the addition of OH to monosubstituted monocyclic aromatics by electrophilic addition in the gas phase became accessible in 1980 and 1981 by determining the rate constants for OH + biphenyl, chlorobenzene, benzonitrile and nitrobenzene by research students who enabled us to determine the reaction constant for gas-phase addition of OH. Together with the rate constants for aniline and phenol determined by Rinke and Wahner this led to the regression $\log(k/\text{cm}^3\text{s}^{-1}) = -11.7 - 1.41 \sigma^+$ for the available literature data (excluding benzaldehyde, where abstraction was known to predominate) (Zetsch, 1982, see below). The extension to disubstituted and polysubstituted monocyclic aromatics then included our own data for *o*- and *m*- dichlorobenzene and 1,2,4-trichlorobenzene and various mono- and polysubstituted benzenes from literature and led to the regression $\log(k/\text{cm}^3\text{s}^{-1}) = -11.6 - 1.39 \sum \sigma^+$. That regression, updated, adopted and properly cited by Kwok and Atkinson (1995), represented the available data within a factor of two and was enabled by the careful selection of the Hammett constants for electrophilic substitution by Brown and Okamoto (1958) from a large number of kinetic experiments in aqueous solution: Solvolysis of *t*-cumylchlorides, bromination, chlorination and nitration of aromatic derivatives, protonolysis of ArylSiMe₃, ionization of Aryl₂CHOH) and IR spectra of acetophenones and by the four "rules" in the conference abstract below. Brown and Okamoto pointed out that this database became extremely consistent if their s^+ values were used rather than the "thermodynamic" s values from equilibria.

It would be most interesting to evaluate the impact of the H bonds on the sum of the Hammett constants for electrophilic addition according to Brown and Okamoto and to

propose revised constants for such combinations of lone-pair substituents with the nitro substituent (if such a consideration is reasonable at all). The very impressive last column of Table 3 then deserves a better resolution than only one digit, and you might wish to extend the data in Table 3 and their discussion to polycyclic aromatics, such as nitronaphthalenes, attempting to estimate/predict the OH-reactivity of nitronaphthols.

The SAR predictions of Table 4, adopting the procedures of Jenkin et al., adjusting the parameters to the experimental data, appear to underpredict the phenols and overpredict the catechols (4M5NCAT remains to be an unexplained extreme case). The different success of the SAR methods needs an additional figure to illustrate this limitation on the basis of the constants for electrophilic addition (and/or those of Jenkin et al.). Additional experimental and theoretical work on this topic is highly encouraged.

Technical corrections and further questions and suggestions are attached.

Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2021-553/acp-2021-553-RC1-supplement.pdf>