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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Stable carbon isotope ratios of ambient secondary organic aerosols in Toronto" *by* M. Saccon et al.

Anonymous Referee #3

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This paper describes the results and interpretations of the analysis of the 13C ratios in samples of selected nitrophenol compounds collected in the particle phase, and in the gas and particle phases together, in Toronto, Canada. Samples were collected in both a summer and winter period. The variation in the 13C ratios of the nitrophenols, in particular with respect to the 13C values of emitted benzene and toluene precursors, but also with respect to season, temperature and gaseous co-pollutant concentrations, are used to derive insight into the likely spatial and temporal scales of the nitrophenol formation.

The paper is generally well written and figures and tables clearly presented.

Scientific comments

The interpretation of the isotope ratio data is predicated on the concept that nitrophenols present in the atmosphere are formed from one reaction pathway, the gas-phase reaction between benzene (or toluene or xylene) and the OH radical; for example: on page 15433 lines 15-20 it is stated "…the aromatic VOC can undergo photo-oxidation with the OH radical…", on page 15435 line 5 it is stated "…nitrophenols are formed from one reaction pathway and are specific to the aromatic VOC + OH reaction"; whilst on page 15439, line 10 it is stated that "Formation of nitrophenols from aromatic VOC is the result of a gas phase reaction sequence….". There is a substantial body of previous work that indicates a potential substantial role for a range of aqueous-phase chemistry in the production of nitrophenols from mono-aromatic precursors. This includes the potential that a portion of nitrophenol measured in the gas phase has re-partitioned back into the gas phase following reaction pathways through the aqueous phase, e.g. through a phenol emitted precursor or a phenol intermediate. The authors have briefly highlighted some of this literature in the second and third paragraphs of the Introduction. In the fourth paragraph of the Introduction (starting p15434, line 12) the authors also refer to primary sources of nitrophenol to the atmosphere from traffic exhausts. So why, having referred to these other sources and reaction pathways to nitrophenol formation, do the authors indicate that their measurements can be interpreted in the context of a single gas-phase reaction of aromatic with OH? Indeed there appears to be a direct contradiction in the opening lines of the Introduction between page 15433, lines 15-20 where it is stated that nitrophenols are dominantly produced by gas-phase reaction with OH, and line 24 where it is stated that 4-nitrophenol has several proposed formation pathways in both gas and aqueous phases. Similarly, on page 15441, line 18, it is stated that "The three methyl nitrophenol isomers we studied are formed from the same precursor following the same initial reaction step, the addition of an OH radical to the aromatic ring of toluene" – this seems to be an assertion, rather than based on direct evidence, for samples collected from the atmosphere (as opposed to a controlled chamber study); the authors themselves cite in the introduction that methyl nitrophenols have been noted to be emitted to the atmosphere from direct emissions from vehicle exhausts. The authors do return to the issue of atmospheric nitrophenols derived from direct emissions rather than via atmospheric oxidation of mono-aromatic VOC, but this is not until the second and third from last paragraphs of the Results and Discussion section, and the direct emissions are largely dismissed as not being important. More clarity on the authors' interpretation in the context of only a gas-phase OH reaction is needed earlier on in the Introduction and during the Results sections.

This reader's attempt to interpret analysis in the context of this sole gas-phase formation pathway was not helped by some unclear phrasing in the description of chemical reactions. As examples. . .(1) on page 15437, lines 13 & 20, and on p15438, line 15, the phrase "initial phase of the reaction" is used. What is meant here by a "phase" (in a kinetic sense) of a reaction? I don't think the authors mean the formation of a transition state in a reaction? The nitrophenol formation pathways are multi-reaction sequences. Perhaps by "phase" the authors mean the first, and/or rate-determining, reaction of a multi-reaction scheme? In each case, the text needs to make clear what chemical reaction is the subject. (2) Likewise, on page 15435, line 12, it is not clear to which reaction the phrase "sum of all reaction products" refers – the generation of a nitrophenol from an aromatic involves more than one reaction. (3) And, again, on page 15435, line 12, I could not work out what actual reaction or reaction(s) are being referred to in the sentence "This allows for a first order prediction of the dependence between isotope ratios of reaction products and photo-chemical precursor processing in the atmosphere".

The understanding of the authors' work would benefit from a schematic of the chemical reaction sequence their study provides information on.

P15443, lines 18-26: Some analysis of results is undertaken with respect to wind direction during a sample collection, but there is little detail on the stability of a wind direction during a sample collection. There is only the sentence "Only samples with a relatively stable wind direction during sampling were used for the analysis"; what criteria actually defines "relatively stable wind direction" and how many samples were retained and excluded from analysis after application of the sample selection? Is this analysis in fact based on only a minority of samples?

Technical comments

P15434, l11: The citation to Hamilton et al. 2005 doesn't look like a correct citation here.

P15442, l23: Better to phrase as "the values actually observed for. . ."

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 15431, 2015.