Atmos. Chem. Phys. Discuss., 5, S912–S916, 2005
www.atmos-chem-phys.org/acpd/5/S912/
European Geosciences Union

Atmospheric
Chemistry
and Physics
Discussions

# *Interactive comment on* "Evaluation of the pathways of tropospheric nitrophenol formation using a multiphase model" *by* M. A. J. Harrison et al.

**M. A. J. Harrison et al.**

Received and published: 25 May 2005

### Author response to referee 1

We thank the referee for their input and are pleased to note they favour publication of the work after consideration of their comments.

**Reply to referee's general comments:**

(1) The fraction, $f_w$, of a soluble species distributed at equilibrium between gas and

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

aqueous phases that is present in the aqueous phase is given by,

$$f_w = 1 - \frac{1}{(1 + L_c HRT)}$$

where $L_c$ is the volumetric liquid water fraction of aqueous phase present, *H* is the Henry's Law coefficient of the species, *R* is the gas constant (in appropriate units: $0.08205 \text{ L atm mol}^{-1} \text{ K}^{-1}$) and *T* is the temperature. Using this equation and the Henry's Law data used in our model (Table A11), we have calculated the values of $f_w$ for 2-nitrophenol and 4-nitrophenol for the two model example temperatures of 278 K and 298 K. The calculated fractions match extremely closely the fractions plotted in Figures 4 and 6 for *T* = 278 K and 298 K, respectively, and described in the text (p. 1124-25). For example, for *T* = 278 K and $L_c = 3 \times 10^{-7}$, the calculated equilibrium $f_w$ values are $0.5\%$ and $2\%$ for the two scenarios of 90:10 or 10:90 2NP:4NP, respectively, whilst the model output values (Fig. 4, text p. 1124) are $0.4\%$ and $1.6\%$, respectively.

Thus, as the referee correctly infers, the nitrophenol products are essentially at their equilibrium phase partitioning ratios and that aqueous phase uptake and reaction are followed by evaporation of the less soluble product. That a significant proportion of observed gas-phase nitrophenol may be produced via the aqueous phase and partition back into the gas phase is one of the key points we emphasise in our work. We will include the above extra data and text in our revised manuscript, as suggested by the referee, in order to emphasise this point more clearly.

(2) In our revised manuscript we will state more clearly that the model assumes that ring-retaining nitration products are the only product of phenol nitration in the aqueous phase. In Section 2.8 of our original text we did already state that the 2- and 4-nitrophenol isomers "are thought to be the main reaction products of the reaction between phenol and $NO_3$" but we will add a reference to the experimental work on which this statement is based (Barzaghi and Herrmann, 2002), and add a note to indicate that a reduced yield of nitrophenols from this reaction would lower the influence of the aque-

ous phase. The evidence from the small literature that does exist on aqueous phase product yields of phenol nitration indicates that ring-retaining pathways dominate.

The gas-phase rate coefficients for reaction of OH with 2- and 4-nitrophenol have been measured, $9 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson, 1994), and estimated, $4.3 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Kwok and Atkinson, 1995), respectively. Using a gas-phase OH radical concentration of $10^6$ cm$^{-3}$ these rate coefficients yield lifetimes for 2- and 4-nitrophenol of $\sim 13$ and $\sim 3$ days, respectively. The measured upper limit to the rate coefficient for the reaction of 2-nitrophenol with $NO_3$ is $2 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson, 1994). Assuming a similar value for the analogous reaction of 4-nitrophenol (no data available), and a gas-phase $NO_3$ radical concentration of $2 \times 10^8$ cm$^{-3}$, yields a lifetime of $> \sim 2$ days, but probably considerably longer. Thus gas-phase loss of the mono-nitrophenols is not relevant to interpretation of the analysis presented here.

The aqueous-phase rate coefficients for reaction of OH with 2- and 4-nitrophenol are $9.2 \times 10^9$ M$^{-1}$ s$^{-1}$ and $3.8 \times 10^9$ M$^{-1}$ s$^{-1}$, respectively (Barzaghi and Herrmann, 2004), which for an average aqueous phase OH concentration of $\sim 10^{-13}$ M yields lifetimes of $\sim 0.3$ h and $\sim 0.7$ h respectively. The corresponding aqueous-phase rate coefficients for reaction with $NO_3$ are $2.3 \times 10^7$ M$^{-1}$ s$^{-1}$ (Barzaghi and Herrmann, 2004) and $7.1 \times 10^7$ M$^{-1}$ s$^{-1}$ (Umschlag et al., 2002), respectively, which for an average $NO_3$ concentration of $\sim 10^{-13}$ M yields lifetimes of $\sim 5$ and $\sim 2$ days, respectively.

Thus, from the above, only the aqueous phase reaction with OH is a fast loss process for the nitrophenol products. However, as demonstrated in the model, nitrophenol product formed in the aqueous phase rapidly equilibrates back into the gas-phase (with a diffusion timescale of seconds or less) so that the majority of it is not subject to loss by the aqueous-phase OH reaction.

(3) It is true that a liquid volume water fraction ($L_c$) of $3 \times 10^{-9}$ is unlikely to consist of droplets as large as $10\ \mu$m in diameter, which is why we already examined scenarios in which the water content is assumed dispersed in droplets of diameter $1\ \mu$m (Fig.

9b). Likewise, we also examined the impact of assuming that the water content is dispersed in droplets of $d = 100\ \mu\mathrm{m}$ (Fig 9a), which is more appropriate for the largest assumed $L_c$ values. The majority of our discussion of model results is focused on the "base scenario" conditions of $L_c = 3 \times 10^{-7}$ and $d = 10\ \mu\mathrm{m}$ which are entirely realistic conditions for the atmosphere, as described in Section 2.6. In our revised manuscript we shall make clear that the lowest $L_c$ values plotted in the figures would be expected to be associated with smaller droplet diameters. (The referee is correct that for very small droplets there will be additional effects such as ionic strength that are not incorporated into the analyses).

Reply to referee's specific comments:

A number of the specific comments are issues of rephrasing for clarity or to avoid ambiguity or apparent contradiction, and these will be addressed in revision. Some additional response from us on a couple of the points raised is given below.

The model was run for a 2-day simulation. This is mentioned in Section 3.5 but will also be included in the model description. The results plotted in the figures are the snapshot time-series output and it is the final output after 2 days that is compared with field observations in Section 3.5 (and Table 2). There is essentially no difference in interpretation if final output is obtained from longer simulation or by integration over the run-time.

The only primary emission data available for nitrophenols are isolated measurements of some vehicle exhausts, reported to be up to the mg $\mathrm{m}^{-3}$ range (Nojima et al., 1983; Tremp et al., 1993). There are no inventory data. It is therefore not possible reliably to estimate how much nitrophenol measured in the atmosphere is derived from primary sources. Whilst primary emissions may be important in the immediate roadside environment, it seems likely that the majority of atmospheric nitrophenol is of secondary origin as described here.

Cited references

Atkinson, R., (1994) Gas-Phase Tropospheric Chemistry of Organic-Compounds, J. Phys. Chem. Ref. Data R1-

Barzaghi, P. and Herrmann, H. (2002) A mechanistic study of the oxidation of phenol by OH/NO2/NO3 in aqueous solution, Phys. Chem. Chem. Phys. 4, 3669-3675

Barzaghi, P. and Herrmann, H. (2004) Kinetics and mechanisms of reactions of the nitrate radical (NO3) with substituted phenols in aqueous solution, Phys. Chem. Chem. Phys. 6, 5379-5388

Kwok, E. S. C. and Atkinson, R. (1995) Estimation of Hydroxyl Radical Reaction-Rate Constants for Gas- Phase Organic-Compounds Using A Structure-Reactivity Relationship - An Update, Atmos. Environ. 29, 1685-1695

Nojima, K., Kawaguchi, A., Ohya, T., Kanno, S. and Hirobe, M. (1983) Studies on Photochemical-Reaction of Air-Pollutants .10. Identification of Nitrophenols in Suspended Particulates, Chemical Pharmaceutical Bulletin 31, 1047-1051

Tremp, J., Mattrel, P., Fingler, S. and Giger, W. (1993) Phenols and nitrophenols as tropospheric pollutants - emissions from automobile exhausts and phase-transfer in the atmosphere, Water Air Soil Pollut. 68, 113-123

Umschlag, T., Zellner, R. and Herrmann, H. (2002) Laser-based studies of NO3 radical reactions with selected aromatic compounds in aqueous solution, Phys. Chem. Chem. Phys. 4, 2975-2982

---

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 1115, 2005.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU