

The manuscript "Dual roles of inorganic aqueous phase on SOA growth from benzene and phenol" provides new insight into the SOA formation processes from the oxidation of gaseous benzene and phenol under various HC:NOx ratios. To date, experimental studies show a negative related NOx dependence of SOA formation yield from the oxidation of aromatic hydrocarbons. The work presented herein combines experimental chamber investigations with a complex modeling system to deeply explore the heterogenous chemistry within SOA particles with respect to various relevant environmental parameters (i.e., acidity of SOA particles, SOA thermodynamical equilibrium, partitioning coefficients, temperature and RH). Authors employed a variety of modeling tools and used available atmospheric databases (MCM, EPI Suite) to design a tool for predicting the SOA mass under different atmospheric conditions by mean of heterogenous reactions in a two media particle system (inorganic/organic liquid phases) and by gas-particle partitioning processes. Acid-catalyzed formation of a persistent phenoxy radical (PPR) in wet inorganic aerosols and its desorption into the gas phase is hypothesized to be responsible for ozone consumption, thus lowering the atmospheric oxidation capacity near human settlements. Significant improvements were made to the in-use UNIPAR model by integrating HOM and H-PPR sequences to accommodate a new gas mechanism driven by the oxidation of benzene and phenol.

Both the experimental and the modeling part are well presented through the manuscript. I recommend this manuscript for publication in ACP after the following concerns are addressed.

Initial manuscript evaluation: Major revisions

You may be more explicit in the abstract about the "Dual roles of inorganic aqueous phase". For instance, "Data presented herein highlights the impact of aqueous phase on SOA generated through benzene and phenol oxidation. The roles of the aqueous phase consist in: (1).... and (2).... .

A discussion regarding minimal incremental reactivity index (MIR) (Carter, 1994/ <https://doi.org/10.1080/1073161X.1994.10467290>) and photochemical ozone creation potentials (Jenkin et al., 2017/ <https://doi.org/10.1016/j.atmosenv.2017.05.024>) of monocycle aromatics would add considerable impact to your current findings and highlight the atmospheric implications.

To what extent would the competing reaction of PPR with the dissolved NO₂ in the inorganic phase affect the UNIPAR/H-PPR model (Kleffmann et al., 1998/ [https://doi.org/10.1016/S1352-2310\(98\)00065-X](https://doi.org/10.1016/S1352-2310(98)00065-X))? Same question for the catechol gas-phase reactions with ozone (Obeid et al., 2024/ <https://doi.org/10.1016/j.envpol.2023.122743>; Coeur-Tourneur et al., 2009/ <https://doi.org/10.1016/j.atmosenv.2008.12.054>; Thomas et al., 2003/ <https://doi.org/10.1002/kin.10121>)

How is $k_{off_phenoxy}$ calculated? Is it assumed to be equal to k_{off_phenol} ? If so, explain why and how an order of magnitude in between the considered value impact the model? Does the model incorporate Leighton equilibrium in predicting the gas-phase O₃, NO₂ and NO concentrations?

Kwok and Atkinson SAR on monocyclic aromatics follows the regression $\log (k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -11.6 - 1.39 \Sigma \sigma^+$, where σ^+ are the Hammett constants for electrophilic substitution by Brown and Okamoto (1958/ <https://doi.org/10.1021/ja01551a055>). If you are using EPI Suite software to estimate the gas kinetic rate coefficients for multi-hydroxy benzenes with vicinal OH groups the software may underestimate the values (Roman et al., 2022/ <https://doi.org/10.5194/acp-22-2203-2022>).

Also, you could calculate and provide in the discussions sections a relative drop in NO₂, O₃ and SOA mass concentration when applying the UNIPAR with and without H-PPR.

Using the current dataset for the UNIPAR/H-PPR, could you estimate the SOA mass distribution from the oxidation of 2-methylphenol and catechol under similar conditions?

Technical corrections, minor questions and suggestions:

Affiliation is not indicated for the authors.

Abstract

L10: gas oxidation or phenol or benzene... > gas oxidation of phenol or benzene...

L25: oxidation, about 53% of the... > oxidation, up to 53% of the...

Across the manuscript you have no consistency expressing the units (i.e., L227: g mol⁻¹, L241: g/L). Choose one way to express the units.

Introduction

L41: oxidation rate (i.e., 1.21571E-12 at 298K) > oxidation rate (i.e., 1.22×10^{-12} cm³ molecule⁻¹ s⁻¹ at 298K) [REFERENCE NEEDED]. Be consistent with the units and the order of magnitude across the manuscript and the supplement material.

L41: but its SOA yield is high > [provide a range for observed SOA formation yield and the corresponding cited paper/papers].

L59: The lifetime is long also due to a p-π conjugated system also help for stabilizing the phenoxy radicals.

L85: delete “^{4-9, 52}”.

L86: of phenol or benzene > of phenol and benzene

Experiment section

L 109: Specify the instrument and the operating conditions used to monitor the HCs concentration presented in Fig 3. What were the sensitivities and the corresponding relative uncertainties for NO/NOx (Villena et al., 2012/ <https://doi.org/10.5194/amt-5-149-2012>) and O₃ (Spicer et al., 2012/ <https://doi.org/10.3155/1047-3289.60.11.1353>) photometers? In what extent these uncertainties would affect the experimental findings?

L 116: Regarding the SOA seeds, were particle diameters the same for all experiments? Do you account for differences in SOA surface concentration in the UNIPAR model?

L 117: sulfate, ammonium, nitrate ion peaks in aerosol. > sulfate, ammonium and nitrate ion signals in aerosol phase.

L 120: species (Sulfate, nitrate... > species (sulfate, nitrate...

UNIPAR SOA model

L153: You stated that “Both organic-phase oligomerization and aqueous reactions of reactive species in inorganic phase yield non-volatile OM in the model”. Except for PPR, right?

HOM Formation

L178: The reaction rate constants > The gas phase reaction rate coefficients

PPR Formation

L183: A citation is needed for the branching ratios.

L222: R is a gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). > R is a gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T the absolute temperature.

L245: k1 number and units. Also, a reference should be cited here for adduct formation.

L276: with H-PPR and without H-PPR. > with H-PPR and without (w/o) H-PPR.

Evaluation of the impact of H-PPR on SOA Formation: aerosol acidity

L306: connected to the > connected to the

Sensitivity of SOA formation to NOx 320 level, Temperature, and RH

L321: temperatures (278K, 288K and 298K) > temperatures (278 K, 288 K and 298 K)

L324: 2022 (between 6:30 AM to 5:30... > 2022 (between 6:30 AM to 5:30...

L336: $2.82 \times 10^{-11} \text{ cm}^3/\text{molecule s}^{-1}$ at 298K > and [REFERENCE IS NEEDED]

L337: $1.2 \times 10^{-12} \text{ cm}^3/\text{molecule s}^{-1}$ >

Conclusion and atmospheric implications

L370: the heterogeneously produced PPR production occurs via.... > the H-PPR occurs via....

L371: OH radical > OH radicals that are

References

L444: New York2002

L460: doi [REMOVE UNDERLINE]

L464: New York2002

L489: doi [REMOVE UNDERLINE]

L493: with NO 2> with NO₂

L510: doi [REMOVE UNDERLINE]

L518: doi [REMOVE UNDERLINE]

L525: the absence of NO_x, the absence of NO₂

L530: doi [REMOVE UNDERLINE]

L541: doi [REMOVE UNDERLINE]

L548: doi [REMOVE UNDERLINE]

L554: p-amino... > p-amino...

L563: doi [REMOVE UNDERLINE]/check doi

L572: doi [REMOVE UNDERLINE]

L580: *m*-xylene/doi [REMOVE UNDERLINE]

What were the wall deposition and the dilution rates for SOA, phenol, ozone and NO₂.

L624 and L625: 4:00 > 16:00 (as in Figs. 3 and 4)

L633: HO₂ RO₂ > HO₂ RO₂

L639: Figure 2: the k_2 decomposition coefficient should be changed to match k_{phenoxy} used in the manuscript body.

L642: k1 subscript

L645: Figure 3 and Figure 4 could be split into two parts, one for phenol and one for benzene. Try to use the same style (denotations, legend) for all the figures presented in Fig 3. and Fig. 4. Some left/right and down ticks would fit decently for all the figures. In Fig 3(B) and 3(C), Fig 3(H) and 3(I) use the same scale for better comparison. There is a different trend of HC in Fig 3 (A), (B), (C) in the first two hours compared with others for phenol. In Fig 3 (G-L) you have some variations. Are those in the uncertainty domain for your measurements? Fit the explanatory text of the experiment in the corresponding figure.

L646: Use subscripts for the inorganic species in figures and also in figure capitulations!

L663: 2 ppb > 2 ppb; L664: 298K > 298 K

L666 and L675: Same observations as in other figures. Figure 7 (C) scale, axis titles and legend color are different. Subscripts for OMAR and OMP to be consistent with the text. 298K > 298 K.

Supplement material

Stoichiometric coefficients

Please verify Eq. 13 > A1, B1, C1, D1 parameters!

Section 4: Check the subscripts for chemical compounds (i.e., H₂O₂) and superscript for units and large numbers. Italic font for notations (i.e., k_{ph})