Manuscript: egusphere-2023-2461

Reviewer #1

General comment. 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:NO$_x$ ratios. To date, experimental studies show a negative related NO$_x$ 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.

Response to the general comment: Thank you for your encouraging feedback on our paper. We have addressed your comments, to show clarity and better comprehension.

Comment 1. 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).

> **Response:** Clarify of dual role of aqueous phase on SOA formation was added in abstract, and reads now,

> "Benzene, emitted from automobile exhaust and biomass burning, is ubiquitous in ambient air. Benzene is a precursor hydrocarbon (HC) that forms secondary organic aerosols (SOA), but its SOA formation mechanism is not well studied. To accurately predict the formation of benzene SOA, it is important to understand the gas mechanisms of phenol, which is one of the major products formed from the atmospheric oxidation of benzene. Our chamber study found that wet-inorganic aerosol (1) retarded the gas oxidation of phenol or benzene, and (2) suppressed SOA formation. To explain the unusual effect of aqueous phase, it is hypothesized that a PPR effectively forms via a heterogeneous reaction of phenol and phenol-related products in the presence of wet-inorganic aerosol. These PPR species are capable of catalytically consuming ozone during a NO_x cycle and negatively influencing SOA growth. In this study, explicit gas mechanisms were derived to produce the oxygenated products from the atmospheric oxidation of phenol and benzene. Gas mechanisms include the existing Master Chemical Mechanism (MCM v3.3.1); the reaction path for peroxy radical adducts originating from the addition of an OH radical to phenols forming low-volatility products (e.g., multi-hydroxy aromatics); and the mechanisms to form heterogeneous production of PPR. The simulated gas products were classified into volatility-reactivity based lumping species and incorporated into the UNIfied Partitioning Aerosol Reaction (UNIPAR) model that predicts SOA formation via multiphase reactions of phenol or benzene. The predictability of the UNIPAR model was examined using chamber data, which were generated for the photooxidation of phenol or benzene under various experimental conditions (NO_x levels, humidity, and inorganic seed types). The SOA formation from both phenol and benzene still increased in the presence of wet inorganic seed because of the oligomerization of reactive organic species in aqueous phase. However, model simulations show a significant suppression in ozone, the oxidation of phenol or benzene, and SOA growth, compared to those without PPR mechanisms. In addition, the production of PPR is accelerated in the presence of acidic aerosol and this weakens SOA growth. In benzene oxidation, up to 53% of the oxidation pathway is connected to phenol formation in the reported gas mechanism. Thus, the contribution of PPR to gas mechanisms is less than phenol. Overall, SOA growth in phenol or benzene is negatively related to NO_x levels in the high NO_x region (HC ppbC/NO_x ppb <5). However, the simulation indicates that the significance of PPR rises with decreasing NO_x levels. Hence, the influence of NO_x levels on the SOA formation from phenol or benzene is complex under varying temperature and seed types. The integration of comprehensive explicit gas mechanisms of phenolic compounds with SOA model will improve the prediction of SOA formation form the oxidation anthropogenic HCs and wildfires smoke."

Comment 2. A discussion regarding minimal incremental reactivity index (MIR) (Carter, 1994/ https://doi.org/10.1080/1073161X.1994.10467290) and photochemical ozone creation potentials (POCP) (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.

> **Response**: The relatively low MIR or POCP values of phenol and benzene can be explained via catalytic consumption of ozone by PPR, we cited paper recommended by the reviewer. This reads below equation R2 in Section 3.2.2 PPR formation in the revised manuscript.

Comment 3. To what extent would the competing reaction of PPR with the dissolved NO_2 in the inorganic phase affect the UNIPAR/H-PPR model (Kleffmann et al., 1998/ 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)

> **Response**: In our mechanism, the reaction of phenoxy radicals (phenol, catechol, and nitrophenols) with NO_2 (R3, R4, and R5) occurs mainly in the gas phase. In the ambient temperature, the partitioning of NO_2 into the inorganic salted aqueous phase is generally low. This reaction would possibly active in the stratospheric atmosphere, where temperature is low (average -50 $^{\circ}$C).

Comment 4. 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 O_3, NO_2 and NO concentrations?

> **Response**: Rate constant $k_{off\_phenoxy}$ was calculated differently from k_{off_phenol} due to their different chemical structure. For example, phenol can be both a donor and an accepter for hydrogen bonding but a phenoxy radical can be an accepter only. k_{off} is calculated by Eq.5 which is influenced by K_{in} and k_{on}. As seen in Eq.3, we assumed that the oxygen radical in the phenoxy radical is treated as a ketone functional group to calculate its vapor pressure and activity coefficient.

Comment 5. Kwok and Atkinson SAR on monocyclic aromatics follows the regression log $(k/cm^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -11.6 – 1.39 \Sigma\sigma+$, where $\sigma+$ 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). '

>**Response**: We use the structure reactivity relationship using the group table. This estimation method can be reliable when it is used in its database, but extrapolation to organic compounds outside of the database results in a lack of the assurance of its accuracy. This reads in at the end of Section 3.2.1.

>"Brown, H. C., Okamoto, Y.: Electrophilic Substituent Constants, J. Am. Chem. Soc., 80, 4979-4987, 10.1021/ja01551a055, 1958"

Comment 6. Also, you could calculate and provide in the discussions sections a relative drop in NO_2, O_3 and SOA mass concentration when applying the UNIPAR with and without H-PPR.

>**Response**: The simulation of gas concentration was described in Fig.3 and discussed in Ln 275 to 279. SOA formation with or without H-PPR was discussed in Fig.4 and lines between 289 to 292.

Comment 7. 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?

>**Response:** Yes, catechol and *o*-cresol are products of the oxidation of benzene (or phenol) and toluene, respectively. In this study, toluene was not included. The oxidation of *o*-cresol for the gas mechanism to form PPR was studied in the previous paper (Choi and Jang, 2022). The oxidation paths of benzene and toluene include the mechanisms of catechol and *o*-cresol.

>"Choi, J. and Jang, M.: Suppression of the phenolic SOA formation in the presence of electrolytic inorganic seed, Science of The Total Environment, 851, 158082, doi:10.1016/j.scitotenv.2022.158082, 2022."

For technical corrections, minor questions and suggestions

Comment: Affiliation is not indicated for the authors.

>**Response:** This has been done.

Abstract

Comment L10: gas oxidation or phenol or benzene… > gas oxidation of phenol or benzene…

Response: This has been done.

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

Response: This has been done.

Comment 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.

Response: This has been done. The units system was unified.

Introduction

Comment L41: oxidation rate (i.e., 1.21571E-12 at 298K) > oxidation rate (i.e., $1.22 \times 10\text{-}12$ 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. but its SOA yield is high > [provide a range for observed SOA formation yield and the corresponding cited paper/ papers].

Response: Reference for benzene oxidation rate was added. Sentence in L42 provides a citation regarding the benzene SOA yield.

"Borrás,E., Tortajada-Genaro, L. A.: Secondary organic aerosol formation from the photo-oxidation of benzene, Atmos. Environ., 47, 154-163, https://doi.org/10.1016/j.atmosenv.2011.11.020, 2012."

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

Response: The information was added.

Comment L85: delete "4-9, 52".

Response: This has been done.

Comment L86 of phenol or benzene > of phenol and benzene

Response: This has been done.

Experiment Section

Comment 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/NO$_x$ (Villena et al., 2012/ https://doi.org/10.5194/amt-5-149-2012) and O$_3$ (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?

Response: It was added to a revised manuscript.

Comment 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?

> **Response:** The geometric mean diameter of seeds is on average 146 nm. In the current UNIPAR model, the surface concentration of seed is not counted. SOA formation is calculated based on aerosol volume.

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

> **Response:** This has been changed.

Comment L 120: species (Sulfate, nitrate… > species (sulfate, nitrate…

> **Response:** This has been changed.

UNIPAR SOA model

Comment 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?

> **Response:** This sentence is not related to PPR formation. The production of PPR influences the gas oxidation and the rate of production of oxygenated products. Ultimately, the retardation of gas oxidation slows down the SOA formation. This reads now in Section 3.1 2),
>
> "…The distribution of products was influenced by H-PPR as a function of the amount of sulfuric acid. H-PPR increases the contribution of fresh product distribution."

HOM Formation

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

> **Response:** We decided to use the term constant instead of coefficient since it includes only numbers.

PPR Formation

Comment L183: A citation needed for branching ratios.

> **Response**: Citations for branching ratio have been added to reference of the revised manuscript.

"Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 181–193, https://doi.org/10.5194/acp-3-181-2003, 2003."

"Bloss, C., Wagner, V., Jenkin, M. E., Volkamer, R., Bloss, W. J., Lee, J. D., Heard, D. E., Wirtz, K., Martin-Reviejo, M., Rea, G., Wenger, J. C., and Pilling, M. J.: Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons, Atmos. Chem. Phys., 5, 641–664, https://doi.org/10.5194/acp-5-641-2005, 2005."

Comment L222: R is a gas constant (8.314 J mol-1 K-1). > R is a gas constant (8.314 J mol-1 K-1) and T the absolute temperature.

> **Response:** This has been changed.

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

> **Response:** We determined the rate constant of *phenol* (*in*) in reacts with the OH radical ($OH(in)$) in in phase to form an intermediate adduct of phenol (*phenol_OH_int* (*in*)) empirically. The sentence reads now,

> "*Phenol* (*in*) in R6 further reacts with the OH radical ($OH(in)$) in *in* phase to form an intermediate adduct of phenol ($phenol\_OH\_int$ (*in*)) at reaction rate constant, k_1 (mol/L) which was determined empirically and very fast. Owing to the fast reaction, the reaction is limited by the concentration of OH radical."

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

> **Response:** This has been changed.

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

Comment L306: connected tothe > connected to the

> **Response:** Typo has been done.

Sensitivity of SOA formation to NO$_x$ 320 level, Temperature, and RH

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

Response: The has been corrected.

Comment L324: 2022 (between 6:30 AM to5:30… > 2022 (between 6:30 AM to 5:30…

Response: This has been corrected.

Comment L336: REFERENCE IS NEEDED

Response: Citations have been added in reference and reads now,

"Yee, L. D., Kautzman, K. E., Loza, C. L., Schilling, K. A., Coggon, M. M., Chhabra, P. S., Chan, M. N., Chan, A. W. H., Hersey, S. P., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from biomass burning intermediates: phenol and methoxyphenols, Atmos. Chem. Phys., 13, 8019–8043, https://doi.org/10.5194/acp-13-8019-2013, 2013."

"Kwok, E. S.C., Atkinson, R.: Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: An update, Atmos. Environ. 29, Issue 14, 1685-1695, https://doi.org/10.1016/1352-2310(95)00069-B, 1995."

Comment L337: 1.2E-12 cm3/molecule s-1 >

Response: The unit has been changed in unified system.

Conclusion and atmospheric implications

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

Response: This has been changed.

Comment L371: OH radical > OH radicals that are

Response: This has been changed.

Comment: What were the wall deposition and the dilution rates for SOA, phenol, ozone and NO$_2$.

    Response: Wall loss factor and dilution rate for SOA, hydrocarbon vapor, and gases were obtained from experimental data. Information were added to footnote of table 1 and reads now,

    e. "The reported SOA mass was corrected for the particle loss to the chamber wall based on the 1st order deposition rate at 64 particle size beans. The dilution rate of SOA is estimated with the gas dilution factor determined using trace gas (CCl$_4$)."

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

    Response: This has been changed.

Comment L633: HO2 ….. RO2 > HO$_2$ ……RO$_2$

    Response: This has been changed.

Comment L639: Figure 2: the k2 decomposition coefficient should be changed to match kphenoxy used in the manuscript body.

    Response: This has been changed.

Comment L642: k1 subscript

    Response: This has been changed.

Comment 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 (denotions, 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 expiatory text of the experiment in the corresponding figure.

    Response: We decided to keep original figures without splitting. For Fig 3(B), (C), (H), and (I), the same scale was used in the revised manuscript.

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

Response: This has been done.

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

Response: This has been done.

Comment 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.

Response: This has been done.

Supplement material

Stoichiometric coefficients

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

Response: This has been done.

Comment on Section 4: Check the subscripts for chemical compounds (i.e., H_2O_2) and superscript for units and large numbers. Italic font for notations (i.e., kph)

Response: This has been done.

Comment on References

L444: New York2002

L460: doi [REMOVE UNDERLINE]

L464: New York2002

L489: doi [REMOVE UNDERLINE]

L493: with NO 2> with NO_2

L510: doi [REMOVE UNDERLINE]

L518: doi [REMOVE UNDERLINE]

L525: the absence of NO_x, the absence of NO_2

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]

Response: These have been done.