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Title: Unveiling the multiphase fate of 2,4-dinitrophenol on aerosols: Interfacial hydration governs competing oxidation pathways and unexpected toxicity amplification

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Dear editor (in *Atmospheric Chemistry and Physics*)

We sincerely thank the Editor and the Reviewer for their careful assessment of our revised manuscript and for the constructive comments and suggestions provided during this second round of review. The remaining comments have helped us further clarify the scope of our conclusions, strengthen the atmospheric interpretation of the calculated kinetics, and more clearly distinguish the direct computational findings from their broader atmospheric and toxicological implications.

In response to these comments, we have carefully revised the manuscript and provide a detailed point-by-point response below. The Reviewer's comments are reproduced in *italics*, followed by our responses in blue text. All changes made during this second revision are indicated using Track Changes in the marked-up manuscript. Page and line numbers cited in our responses refer to the marked-up second revised manuscript.

Yours sincerely,

Jianfei Sun

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Response to Referee

General Comments

The manuscript has improved substantially since the first review, particularly regarding literature coverage, discussion of model limitations, and treatment of NO_2 chemistry. However, several conclusions remain stronger than warranted by the evidence presented. The remaining concerns primarily involve overinterpretation of atmospheric significance, the strength of the toxicity claims derived from QSAR predictions, and limited integration of recent experimental literature on heterogeneous oxidation and nighttime nitrate-radical chemistry. These issues appear addressable through a focused revision and do not require fundamental changes to the overall structure of the manuscript. Addressing the remaining concerns would substantially strengthen the scientific impact of the work and help establish it as a more robust and meaningful contribution to the field. I therefore recommend major revision to address the comments below.

Response to General Comments: We sincerely thank the referee for the careful second-round assessment and for recognizing the substantial improvements in literature coverage, model limitations, and treatment of NO_2 chemistry. We agree that several statements in the previous revision extended beyond what can be supported by the present DFT, MD, and QSAR framework. We have therefore carried out a focused revision throughout the title, Abstract, Introduction, kinetic discussion, interfacial

discussion, ecotoxicity section, and Conclusions. Specifically, we (i) removed unsupported statements concerning atmospheric residence time, long-range transport, air-quality-model underestimation, and regulatory implications; (ii) replaced claims of toxicity or environmental-risk amplification with the more precise language of predicted changes in toxicity indicators; (iii) expanded the discussion of nighttime NO_3 chemistry and explicitly defined NO_3 oxidation as an important pathway outside the scope of the present calculations; and (iv) strengthened the kinetic interpretation using pseudo-first-order loss estimates and corresponding diagnostic lifetimes while clarifying that these estimates do not constitute a complete atmospheric lifetime budget. These changes substantially narrow the atmospheric claims and align the conclusions with the evidence actually provided by the computational framework.

Response to Major Comments

Comment 1: *The manuscript continues to draw conclusions regarding atmospheric residence time, long-range transport, air-quality model underestimation, and regulatory relevance that are not supported by the computational framework employed. The MD simulations provide molecular-level information on adsorption behavior in an idealized system but do not constrain atmospheric lifetimes, transport, or large-scale environmental impacts. These statements should be removed, substantially qualified, or supported by additional quantitative atmospheric analysis.*

Response: We thank the Reviewer for this important comment and agree that some statements in the previous version could be interpreted as extending beyond

what can be supported by the present MD simulations. The simulations were designed to examine the adsorption configurations and interaction energies of 2,4-DNP in an idealized C60/water system. Processes required to quantitatively determine atmospheric residence time and transport, including gas–particle partitioning, aerosol liquid water content, particle phase state, deposition, and atmospheric transport, are not represented in the current model. We have therefore systematically reconsidered the relevant statements throughout the manuscript. The proposed link between hydration-dependent adsorption and longer atmospheric residence time or enhanced long-range transport under dry conditions has been removed. Statements concerning possible underestimation of health risks by current air-quality models and the need for regulatory attention have also been deleted, because these implications cannot be established from the present calculations. The discussion in Section. 3.2 has been revised accordingly to more clearly define the scope of the MD results. Hydration effects are now interpreted only in terms of adsorption configurations and interaction strengths within the idealized model system. We explicitly state that the present MD simulations do not quantitatively constrain atmospheric residence time, gas-particle partitioning, or long-range transport. Quantitative evaluation of these quantities would require additional partitioning calculations and atmospheric chemical and transport modeling incorporating relevant aerosol properties and atmospheric processes, which are beyond the scope of the present study.

Author's changes in manuscript: **(1) Restricted scope of the Abstract to molecular-level computational findings (L22–L42):** "This study elucidates the

mechanisms of selected transformation pathways of 2,4-dinitrophenol (2,4-DNP) using an integrated computational framework. In the gas phase, the calculated initial reactions with hydroxyl radicals (•OH) and ozone (O_3) are kinetically more favorable than the direct reaction with nitrogen dioxide radical (•NO_2), which is kinetically hindered. In the aqueous phase, solvation substantially modifies the calculated reaction kinetics, and the cumulative electron-withdrawing effect of the two nitro substituents lowers the O_3 reaction rate coefficient by approximately three orders of magnitude relative to mononitrocatechol. For the key radical intermediate generated by •OH addition, hydrogen atom abstraction (HAA) by O_2 is kinetically favored over the competing •NO_2 pathway, based on the calculated barriers and an illustrative comparison of effective rates under representative atmospheric concentrations. At the gas-aqueous interface, molecular dynamics (MD) simulations show a non-monotonic dependence of 2,4-DNP adsorption on hydration in the idealized C60/water system, with adsorption strengthening at moderate hydration and weakening at high hydration. Finally, QSAR calculations predict that certain ozonolysis products exhibit higher predicted Ames mutagenicity and developmental toxicity indicators than the parent compound, indicating product-specific changes in toxicity profiles during oxidation. These screening-level predictions require experimental validation. These findings provide mechanistic insights into selected transformation pathways and interfacial interactions of 2,4-DNP and motivate further experimental investigation of its transformation products and their toxicological properties.” **(2) Atmospheric interpretation of the calculated kinetics restricted to the investigated reaction**

channels (L468–L474, L488–L494): "These bimolecular rate coefficients describe the intrinsic reactivity of the investigated pathways, but do not by themselves determine their atmospheric importance, which also depends on oxidant concentrations and phase partitioning. To examine whether the very low intrinsic reactivity of the direct •NO_2 pathway could be offset by nighttime •NO_2 accumulation, pseudo-first-order rate coefficients were estimated under illustrative scenarios based on literature-reported oxidant concentrations." "Therefore, under the illustrative nighttime conditions considered here, the direct •NO_2 pathway remains more than seven orders of magnitude slower than the •OH pathway and is unlikely to compete effectively with •OH oxidation. Importantly, these estimates compare only the investigated bimolecular reaction channels and do not represent the overall atmospheric lifetime of 2,4-DNP, which would also depend on photolysis, deposition, phase partitioning, heterogeneous chemistry, and other loss processes." **(3) Aqueous-phase rate coefficients restricted to intrinsic reactivity rather than direct atmospheric importance (L494–L509):** "The aqueous-phase calculations further indicate appreciable intrinsic reactivity toward O_3. Accordingly, the relative contributions of the investigated pathways to the overall atmospheric loss of 2,4-DNP cannot be quantified without additional partitioning information and atmospheric chemistry modeling. The possible involvement of •NO_2 in subsequent reactions with primary oxidation intermediates is discussed separately below.

The atmospheric contribution of aqueous-phase reactions also depends on the fraction of 2,4-DNP present in the aqueous phase. The Henry's law constant for

2,4-DNP has been reported as 5.70 × 10^{-8} atm·m^3/mol at 5 °C (Lütt*k*e and Levsen, 1997). Its acid dissociation constant (pKa ≈ 4.09 at 25 °C) further affects aqueous partitioning because the deprotonated form is more water-soluble than the neutral species (Schwarzenbach et al., 1988). Aerosol liquid water content also determines the aqueous volume available for multiphase reactions. Without quantitative information on these partitioning parameters under specific atmospheric conditions, the aqueous-phase rate constants should be interpreted as intrinsic reactivity indicators rather than direct measures of atmospheric importance." **(4) MD interpretation restricted to molecular-scale adsorption in the idealized C60/water/2,4-DNP system (L719–L732):** "The MD simulations presented here are restricted to molecular-scale adsorption behavior in the idealized C60/water/2,4-DNP system. The results provide insights into how hydration modulates specific non-covalent interactions, but they do not account for key aerosol properties that govern humidity-dependent behavior in real atmospheric particles, including liquid water content, ionic strength, phase behavior, viscosity, and particle morphology. These properties vary with relative humidity, particle composition, and atmospheric conditions, thereby influencing particle physical state and water uptake. The simulations therefore represent a simplified model system. The MD results should be interpreted as molecular-scale insights into adsorption behavior rather than as direct predictions of atmospheric persistence or humidity-dependent partitioning. The present simulations do not quantitatively constrain atmospheric residence time, gas-particle partitioning, or long-range transport. These quantities require additional

partitioning calculations and atmospheric chemistry and transport modeling." **(5) atmospheric residence-time and long-range-transport implications explicitly excluded from the Conclusions (L835–L839, L856–L860, L864–L869):** "These MD results represent molecular-scale behavior within the idealized model system and do not provide quantitative constraints on atmospheric residence time, gas-particle partitioning, or long-range transport. QSAR predictions indicate that certain ozonolysis products exhibit higher predicted Ames mutagenicity and developmental toxicity than the parent compound." "Moreover, quantitative determination of the relative contributions of the investigated pathways to the atmospheric loss of 2,4-DNP would require atmospheric chemistry modeling that incorporates temporally resolved oxidant concentrations, gas-particle and gas-aqueous partitioning, aerosol liquid water content, and additional loss processes." "Future work should therefore focus on experimental validation of the calculated reaction kinetics and QSAR predictions, more realistic representations of carbonaceous aerosol surfaces, and atmospheric chemistry modeling that explicitly incorporates phase partitioning and relevant loss processes. Within these limitations, the present results provide molecular-level mechanistic insight that can guide future experimental and modeling studies of nitrophenol multiphase chemistry."

Comment 2: *Although the revised manuscript acknowledges the limitations of QSAR predictions, the title, abstract, and conclusions continue to imply demonstrated toxicity amplification and environmental risk amplification. Because the toxicity analysis remains based entirely on predictive models without experimental validation,*

product yields, or exposure estimates, the results should be presented consistently as predicted changes in toxicity indicators rather than demonstrated increases in environmental risk. Ensure that conclusions clearly distinguish computational findings from broader atmospheric implications.

Response: We thank the reviewer for this important clarification. We agree that the QSAR results represent screening-level computational predictions and cannot demonstrate toxicity amplification or increased environmental risk. We have therefore consistently restricted the toxicity-related conclusions throughout the manuscript, including the title, Abstract, Results and Discussion, and Conclusions, to predicted toxicity indicators. The revised manuscript explicitly distinguishes compound-level QSAR predictions from environmental or health risk and states that assessment of the latter would require information on product yields, environmental concentrations and exposure, and experimentally validated toxicity. The revised manuscript also explicitly states the limitations of the QSAR analysis and the need for experimental validation.

Author's changes in manuscript: **(1) Toxicity claim in the title restricted to predicted changes in toxicity indicators (L1–L3):** "Unveiling the multiphase fate of 2,4-dinitrophenol on aerosols: Interfacial hydration modulates competing oxidation pathways and predicted toxicity indicators" **(2) Toxicity conclusions in the Abstract restricted to screening-level QSAR predictions (L36–L42):** "Finally, QSAR calculations predict that certain ozonolysis products exhibit higher predicted indicators of Ames mutagenicity and developmental toxicity than the parent

compound, suggesting product-specific changes in predicted toxicity profiles during oxidation. These screening-level predictions require experimental validation. These findings provide molecular-level mechanistic insights into selected transformation pathways and interfacial interactions involving 2,4-DNP and motivate further experimental investigation of its transformation products and their toxicological properties." **(3) Toxicity analysis reframed as predicted toxicity indicators in Section 3.3 (L734, L738–L746, L773–L779):** "3.3 Predicted toxicity indicators" "By focusing on the O_3 pathway, this study provides a defined set of reactions for examining predicted changes in toxicity indicators along this specific transformation products. The conclusions drawn here may provide a useful reference for future investigations of the more complex atmospheric oxidation networks involving radicals such as •OH and •NO_2. Accordingly, the key intermediates and final products (IM17, IM25, IM44, IM54, P1–P4) identified in Figure S2 were predicted using the T.E.S.T. tool (Epa, 2020) to predict Ames mutagenicity and developmental toxicity indicators and to examine changes in predicted toxicity indicators along this specific oxidation process." "Overall, the QSAR analysis predicts that some ozonolysis products exhibit higher predicted indicators of Ames mutagenicity and/or developmental toxicity than the parent, 2,4-DNP. These compound-level predictions describe changes in modeled toxicity indicators and should not be interpreted as demonstrating increased environmental or health risk, which would additionally require information on product yields, environmental concentrations, exposure, and experimentally validated toxicity." **(4) QSAR conclusions restricted to**

screening-level assessment and hypothesis generation (L815–L819): "Overall, the findings should be interpreted as hypothesis-generating(Vom Eyser et al., 2013). Experimental validation through in vitro Ames tests and zebrafish embryo development toxicity assays would be valuable for evaluating the QSAR-predicted toxicity indicators of selected transformation products." **(5) Increased environmental risk explicitly excluded from the Conclusions (L838–L843):** "QSAR predictions indicate that certain ozonolysis products exhibit higher predicted indicators of Ames mutagenicity and developmental toxicity than the parent compound. These results represent compound-level, screening-level predictions and do not establish increased environmental risk, which would require information on product yields, exposure, and experimentally validated toxicity."

Comment 3: *The treatment of nighttime oxidation chemistry remains incomplete. The manuscript draws atmospheric conclusions regarding the fate and transformation of 2,4-DNP while providing only limited consideration of NO3 radical chemistry, despite its recognized importance in the nighttime processing of phenolic compounds. This omission limits the atmospheric interpretation of the proposed reaction framework. The discussion should more clearly place the results within the broader context of known nighttime oxidation processes and relevant experimental studies demonstrating NO3-driven formation of nitrocatechols, oligomers, and brown carbon in phenolic systems (Rana and Guzman, ACS Earth Space Chemistry, 2026, DOI: 10.1021/acsearthspacechem.6c00226) and heterogeneous oxidation pathways in phenolic aldehydes (Rana and Guzman, ACS Physical Chemistry Au, 2026, DOI:*

10.1021/acsphyschemau.6c00106)

Response: We thank the Reviewer for this important comment and for drawing our attention to these recent experimental studies. We agree that the previous manuscript did not sufficiently place the investigated reaction pathways within the broader context of nighttime oxidation chemistry. The present study examines selected reaction channels involving •OH, O_3, and •NO_2, but does not include direct NO_3-radical oxidation of 2,4-DNP. Therefore, the investigated pathways should not be interpreted as providing a complete description of the nighttime atmospheric transformation of 2,4-DNP. In the revised manuscript, we have expanded the discussion of nighttime oxidation processes and incorporated the suggested recent studies by Rana and Guzman (2026). These experimental studies demonstrate that nighttime heterogeneous oxidation of related phenolic systems can involve NO_3-driven chemistry and yield nitrated and oligomeric products, including nitrocatechols and brown-carbon chromophores. We now explicitly discuss these findings as evidence that NO_3-driven oxidation and subsequent heterogeneous and multiphase processing represent potentially important nighttime pathways for phenolic compounds that are not included in the present computational framework. Accordingly, we have revised statements that could be interpreted as implying a comprehensive assessment of nighttime atmospheric fate of 2,4-DNP. In particular, the pseudo-first-order comparison between •OH and direct •NO_2 reactions is now explicitly limited to the reaction channels investigated in this study and is no longer used to infer the overall nighttime transformation of 2,4-DNP. We also identify direct

NO_3 oxidation and subsequent aging processes as important topics for future kinetic, mechanistic, and experimental investigations. These revisions more clearly define the scope of the present calculations and place our results within the broader context of known nighttime phenolic oxidation chemistry of phenolic compounds.

Author's changes in manuscript: **(1) Nighttime chemistry expanded to include the missing NO_3-driven pathway and recent experimental evidence (L113–L121):** "•NO_3 radicals represent an additional important component of nighttime phenolic chemistry that is not explicitly included in the present computational framework (Rana and Guzman, 2022b; Ng et al., 2017). Recent experimental studies have shown that heterogeneous NO_3 oxidation of catechol can generate nitrocatechols, oligomeric products, and light-absorbing brown-carbon chromophores (Rana and Guzman, 2026b), while related studies of phenolic aldehydes further underscore the complexity of heterogeneous nighttime oxidation pathways (Rana and Guzman, 2026a). These studies underscore the importance of NO_3-driven chemistry in the nighttime transformation of phenolic compounds." **(2) Nighttime interpretation explicitly limited to the investigated O_3, •OH, and •NO_2 pathways (L121–L123):** "The present study, however, is restricted to the reaction pathways initiated by O_3, •OH, and •NO_2; therefore, it does not provide a complete description of the nighttime oxidation chemistry of 2,4-DNP."

Comment 4: *The kinetic discussion remains largely based on comparison of bimolecular rate constants. Inclusion of pseudo-first-rder loss estimates, representative atmospheric oxidant concentrations, or simple lifetime calculations*

would substantially strengthen the connection between the computed kinetics and atmospheric significance.

Response: We thank the Reviewer for this helpful suggestion. To strengthen the connection between the calculated bimolecular kinetics and atmospherically relevant conditions, we have added pseudo-first-order rate estimates using representative atmospheric oxidant concentrations reported in the literature. Specifically, the pseudo-first-order rate coefficients were estimated as $k' = k[X]$, allowing the calculated bimolecular rate coefficients to be interpreted in the context of representative oxidant abundances. Under the concentration scenarios considered, the pseudo-first-order rate coefficient for the direct $\bullet NO_2$ reaction is more than seven orders of magnitude smaller than that estimated for the •OH pathway, indicating that direct reaction with $\bullet NO_2$ is unlikely to compete effectively with •OH oxidation under these specific scenarios. These estimates have been incorporated into the revised kinetic discussion. We further clarify that these pseudo-first-order estimates are intended as scenario-based comparisons of the investigated bimolecular reaction channels, rather than estimates of the overall atmospheric lifetime of 2,4-DNP. A quantitative atmospheric lifetime would additionally depend on photolysis, deposition, phase partitioning, heterogeneous chemistry, $\bullet NO_3$ oxidation, and other loss processes that are not fully represented in the present framework. The revised manuscript now explicitly distinguishes these pathway-specific kinetic estimates from a comprehensive atmospheric lifetime assessment.

Author's changes in manuscript: **(1) Bimolecular kinetics extended to pseudo-first-order atmospheric comparisons for parent 2,4-DNP (L469–L475, L483-L491):** "These bimolecular rate coefficients describe the intrinsic reactivity of the investigated pathways but do not by themselves determine their atmospheric importance, which also depends on oxidant concentrations and phase partitioning. To examine whether the very low intrinsic reactivity of the direct $\bullet NO_2$ pathway could be offset by nighttime $\bullet NO_2$ accumulation, pseudo-first-order rate coefficients were estimated under illustrative scenarios based on literature-reported oxidant concentrations." "Using these literature-reported concentrations as illustrative nighttime scenarios, the pseudo-first-order rate constant for the •OH pathway is estimated to be approximately $10^{-10} \sim 10^{-9}$ s^{-1}, based on $k_{OH} = 3.18 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}. In contrast, for the direct $\bullet NO_2$ pathway, a bimolecular rate coefficient of $k_{NO2} \approx 10^{-28}$ cm^3 $molecule^{-1}$ s^{-1} combined with a nighttime $\bullet NO_2$ concentration of several ppb, yields a pseudo-first-order rate coefficient on the order of 10^{-17} s^{-1}. Therefore, under the illustrative nighttime conditions considered here, the direct $\bullet NO_2$ pathway remains more than seven orders of magnitude slower than the •OH pathway and is unlikely to compete effectively with •OH oxidation." **(2) Pseudo-first-order estimates explicitly separated from the overall atmospheric lifetime (L491–L500):** "Importantly, these estimates compare only the investigated bimolecular reaction channels and should not be interpreted as the overall atmospheric lifetime of 2,4-DNP, which would also depend on photolysis, deposition, phase partitioning, heterogeneous chemistry, and other loss processes. The aqueous-phase calculations further indicate

appreciable intrinsic reactivity toward O_3. Accordingly, the relative contributions of the investigated pathways to the overall atmospheric loss of 2,4-DNP cannot be quantified without additional information on phase partitioning and more comprehensive atmospheric chemistry modeling. The possible involvement of $\bullet NO_2$ in subsequent reactions with primary oxidation intermediates is discussed separately below.**" (3) IM3' competition evaluated using pseudo-first-order effective rates and representative atmospheric oxidant abundances (L593–L601, L604–L614):** "To illustrate this competition, effective pseudo-first-order rates (k × [oxidant]) were estimated using representative atmospheric concentrations and literature-based rate coefficients. The atmospheric concentration of O_2 was taken as 5.4×10^{18} molecules cm^{-3} (0.21 atm). For the reaction of IM3' with O_2 via HAA (calculated barrier = 2.86 kcal mol^{-1}), rate constants for analogous radical + O_2 reactions are typically in the range of $10^{-12} \sim 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (Miyoshi et al., 1990; Morgan et al., 1982). Using a conservative estimate of $k_{O2} \approx 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} gives an effective pseudo-first-order rate coefficient of $k'_{O2} \approx 10^{-12} \times 5.4 \times 10^{18} \approx 5.4 \times 10^6$ s^{-1}, corresponding to an illustrative reaction timescale of approximately 0.2 μs." "For the reaction of IM3' with $\bullet NO_2$ via HAA (barrier = 2.01 kcal mol^{-1}), assuming a representative nighttime $\bullet NO_2$ concentration of $10^{10} \sim 10^{11}$ molecules cm^{-3} and a literature-based rate coefficient of $k_{NO2} \approx 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} gives $k'_{NO2} \approx 10^{-1} \sim 1$ s^{-1}, corresponding to an illustrative reaction timescale of approximately 1 ~ 10 s. Under these assumptions, the effective O_2 reaction rate exceeds that of the investigated $\bullet NO_2$ pathway by more than six orders of magnitude. Thus, although the

low calculated barrier demonstrates the mechanistic feasibility of the indirect $\bullet NO_2$ pathway, this illustrative effective-rate comparison suggests that reaction with O_2 would strongly outcompete the investigated $\bullet NO_2$ pathway under the conditions considered here. Quantifying the atmospheric branching of IM3' would require reaction-specific rate coefficients and a more complete treatment of competing loss processes."

The main detailed revision is listed in the Language Revision Comparison Table in the text.

Line	Origin	Now	Action
L1-L4 (Title)	Unveiling the multiphase fate of 2,4-dinitrophenol on aerosols: Interfacial hydration modulates competing oxidation pathways and predicted increase in toxicity	Unveiling the multiphase fate of 2,4-dinitrophenol on aerosols: Interfacial hydration modulates competing oxidation pathways and predicted toxicity indicators	Changed
L23-76 (Abstract)	This study elucidates the atmospheric transformation mechanisms of 2,4-dinitrophenol (2,4-DNP) using an integrated computational framework. In the gas phase, initial oxidation by hydroxyl radicals (•OH) and ozone (O_3) is identified as the dominant pathway, whereas the direct	This study elucidates the mechanisms of selected transformation pathways of 2,4-dinitrophenol (2,4-DNP) using an integrated computational framework. In the gas phase, the calculated initial reactions with hydroxyl radicals (•OH) and ozone (O_3) are kinetically more favorable than the	Changed

	reaction with nitrogen dioxide radical ($\bullet NO_2$) is kinetically hindered. In the aqueous phase, solvation effects suppress the reaction rates, while the two nitro substituents exert a cumulative electron-withdrawing effect that reduces the rate constant by three orders of magnitude relative to mononitrocatechol. For the key radical intermediate generated by •OH addition, hydrogen atom abstraction (HAA) with O_2 represents the dominant atmospheric fate based on the calculated barriers and the overwhelming concentration advantage of O_2 over $\bullet NO_2$. At the gas-aqueous interface,	direct reaction with nitrogen dioxide radical ($\bullet NO_2$), which is kinetically hindered. In the aqueous phase, solvation substantially modifies the calculated reaction kinetics, and the cumulative electron-withdrawing effect of the two nitro substituents lowers the O_3 reaction rate coefficient by approximately three orders of magnitude relative to mononitrocatechol. For the key radical intermediate generated by •OH addition, hydrogen atom abstraction (HAA) by O_2 is kinetically favored over the competing $\bullet NO_2$ pathway, based on the calculated barriers and an illustrative	

	molecular dynamics (MD) simulations demonstrate that the adsorption of 2,4-DNP onto the C60 aerosol surrogate is non-monotonically modulated by interfacial hydration—first strengthening at moderate hydration and weakening at high hydration. Finally, computational toxicology predicts that certain ozonolysis products exhibit elevated Ames mutagenicity and developmental toxicity indicators relative to the parent compound, suggesting that oxidative processing of 2,4-DNP may not lead to simple detoxification. These findings provide	comparison of effective rates under representative atmospheric concentrations. At the gas-aqueous interface, molecular dynamics (MD) simulations show a non-monotonic dependence of 2,4-DNP adsorption on hydration in the idealized C60/water system, with adsorption strengthening at moderate hydration and weakening at high hydration. Finally, QSAR calculations predict that certain ozonolysis products exhibit higher predicted Ames mutagenicity and developmental toxicity indicators than the parent compound, indicating product-specific changes in toxicity	

	mechanistic insights into the atmospheric transformation pathways of this specific dinitrophenol and highlight the importance of evaluating transformation product toxicity in the environmental risk assessment of nitrophenolic compounds.	profiles during oxidation. These screening-level predictions require experimental validation. These findings provide mechanistic insights into selected transformation pathways and interfacial interactions of 2,4-DNP and motivate further experimental investigation of its transformation products and their toxicological properties	
L77-L82 (Introduction)	Atmospheric aerosols, as pivotal regulators of the Earth's climate system and environmental quality, have long placed the complex study of their physicochemical processes at the forefront of scientific	The complex physicochemical processes of atmospheric aerosols are central to understanding their roles in climate and environmental quality	Changed

	inquiry		
L95-L98 (Introduction)	high Henry's law constant and low vapour pressure lead to significant partitioning into condensed phases such as aerosol particles and cloud/fog droplets	low volatility and favorable aqueous partitioning promote its presence in condensed phases such as aerosol water and cloud/fog droplet	Changed
L100-L101 (Introduction)	comprehensive	molecular-level	Changed
L102-L104 (Introduction)	accurate risk assessment and fate prediction	improving mechanistic descriptions of its environmental transformation and for informing future fate and risk assessments	Changed
L136-L137 (Introduction)	an ideal model	a well-defined model system	Changed
L140 (Introduction)	precisely probe	systematically examine	Changed
L151-L166 (Introduction)	and while •NO_3 chemistry is an important nighttime pathway for phenols(Rana and Guzman, 2022b; Ng et al., 2017), the present study focuses on the	•NO_3 radicals represent an additional important component of nighttime phenolic chemistry that is not explicitly included in the present computational framework(Rana and	Changed

	thermal oxidation network initiated by O_3, •OH, and •NO_2. These differences in concentrations, reactivities, and reaction mechanisms of these species collectively shape the diverse transformation pathways of nitroaromatics under varying diurnal and pollution regimes.	Guzman, 2022b; Ng et al., 2017). Recent experimental studies have shown that heterogeneous NO_3 oxidation of catechol can generate nitrocatechols, oligomeric products, and light-absorbing brown-carbon chromophores(Rana and Guzman, 2026b), while related work on phenolic aldehydes further demonstrates the potential complexity of heterogeneous nighttime oxidation pathways(Rana and Guzman, 2026a). These studies highlight NO_3-driven chemistry as an important process to consider when interpreting the nighttime transformation of phenolic compounds.	

		The present study, however, is restricted to the reaction pathways initiated by O_3, •OH, and $•NO_2$; therefore, it does not provide a complete description of the nighttime oxidation chemistry of 2,4-DNP.	
L205 (Introduction)	the competing	selected	Changed
L207 (Introduction)		a; conditions	Added
L208-L212 (Introduction)	the toxicity evolution of its transformation products. The results provide a molecular-level foundation for a comprehensive assessment of the atmospheric fate and ecological risk of 2,4-DNP	predicted toxicity indicators of its transformation products. The results provide molecular-level insights into selected transformation pathways and interfacial interactions of 2,4-DNP	Changed
L225-L226 (2.1 Density functional theory)	The reaction energies	The reaction energies	Changed

L227 (2.1 Density functional theory)	are	were	Changed
L227 (2.1 Density functional theory)		the	Added
L252-L253 (2.2 Molecular dynamics simulations)	mimic a realistic aerosol multi-phase interface	construct an idealized gas-aqueous interfacial model	Changed
L313 (3.1.1 Characterization of the electronic structure of 2,4-DNP)	indicates that	reveals	Changed
L315 (3.1.1 Characterization of the electronic structure of 2,4-DNP)	values	—a value	Changed
L315-L316 (3.1.1	bonds	bonding	Changed

Characterization of the electronic structure of 2,4-DNP)			
L329 (3.1.1 Characterization of the electronic structure of 2,4-DNP)	sites		Deleted
L338-L347 (3.1.1 Characterization of the electronic structure of 2,4-DNP)	•OH displays dual reactivity: it adds to nucleophilic blue regions on the benzene ring, while also abstracting hydrogen atoms from weakly electrophilic sites such as the C–H bonds (adjacent to nitro groups) or the hydroxyl hydrogen, which correspond to regions of weaker Δfω positive values. Similarly, •NO_2, possessing both radical	•OH and •NO_2 can participate in both ring addition and hydrogen-abstraction reactions. However, the preferred HAA sites cannot be inferred solely from the ground-state Δfω distribution and are evaluated explicitly from the calculated reaction energetics below.	Changed

	and electrophilic characteristics, displays dual reactivity, participating either in radical addition to nucleophilic carbons or in hydrogen abstraction reactions, with its preference modulated by the local Δfω distribution.		
L352-L354 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	revealing transformation mechanisms of 2,4-DNP in the atmosphere.	characterizing the selected transformation pathways examined in this study	Changed
L392-L396 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	The C5–H bond is significantly weakened by the electron withdrawing effect of the adjacent nitro group, making it the preferred abstraction site despite its low electron density.	The preference for C5 abstraction is therefore more appropriately interpreted in terms of the calculated reaction energetics and transition-state structure rather than the ground-state electron-density distribution alone.	Changed

L397-L399 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	•NO_2 is primarily a radical species with only weak electrophilic character. Its addition to the ring is therefore not simply governed by electrophile-nucleophile interactions, but rather by radical stability and transition state polar effects.		Deleted
L402-L403 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	two fundamental elementary steps	radical addition and hydrogen abstraction	Changed
L403 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	exist	are observed	Changed
L406-L408 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and	This reaction mode resembles the •OH-addition process, suggesting some consistency in	This regioselectivity is similar to that calculated for •OH addition.	Changed

•NO_2)	regioselectivity.		
L409-L439 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	are well correlated with the Δfω distribution, •NO_2 is primarily a radical species with only weak electrophilic character. Its addition to the ring is therefore not simply governed by electrophile–nucleophile interactions, but rather by radical stability and transition-state polar effects. The HAA pathway displays markedly different behavior. Unlike •OH, which mainly abstracts hydrogen atoms from the C5 site, •NO_2 preferentially abstracts the hydrogen atom of the hydroxyl group through transition state TS7*. This difference originates from the fundamentally different reaction characteristics	sites show a clearer relationship with the Δfω distribution, •NO_2 has only weak electrophilic character, and its addition pathway cannot be interpreted solely in terms of electrophile–nucleophile interactions. Radical stabilization and transition-state effects may also contribute to the calculated regioselectivity. The HAA pathway exhibits different site selectivity. Whereas •OH preferentially abstracts the C5-bound hydrogen in the gas phase, the lowest-energy HAA channel identified for •NO_2 involves abstraction of the C6-bound hydrogen	Changed

	of the two radicals. The high reactivity of •OH allows it to overcome unfavorable ground-state electrostatics and abstract the H atom at C5. By contrast, $•NO_2$ has much weaker electrophilicity and lower reactivity; its hydrogen abstraction depends on electrostatic complementarity and charge transfer, and it preferentially targets the hydroxyl hydrogen(Shenghur et al., 2014). Moreover, the $•NO_2$-mediated hydrogen abstraction is often accompanied by substantial charge transfer, with a mechanism that more closely resembles proton-coupled electron transfer (PCET)(Tyburski et al.,	through transition state TS10*. Nevertheless, this preference should be distinguished from the overall kinetic feasibility of the pathway. The calculated gas-phase barrier for C6 hydrogen abstraction by $•NO_2$ is 41.39 kcal mol^{-1}, substantially higher than the 18.48 kcal mol^{-1} barrier for the competing C3-addition pathway. Thus, although C6 is the preferred H-abstraction site among the investigated direct $•NO_2$ HAA channels, direct HAA by $•NO_2$ remains kinetically unfavorable for parent 2,4-DNP.	

	2021). In 2,4-DNP, the intramolecular hydrogen bond between the hydroxyl group and the ortho-nitro group significantly weakens the O–H bond, lowering its bond dissociation energy, which further favors hydroxyl hydrogen abstraction by $•NO_2$.		
L451-L452 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and $•NO_2$)	relatively low	calculated	Changed
L452-L453 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and $•NO_2$)	ensures that the reaction remains kinetically feasible in both environmental media	remains moderate within the present reaction framework	Changed
L454-L456 (3.1.2 Primary reactions of 2,4-DNP with	kinetics, consistent with its role as the major atmospheric oxidant	calculated kinetics than the O_3 and direct $•NO_2$ reactions examined here	Changed

O_3, •OH, and •NO_2)			
L459 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	these two •OH-initiated	both	Changed
L460 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	are	may be	Changed
L460-L461 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	and are expected to occur concurrently under atmospheric conditions.	at the molecular level	Changed
L468 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	great	much	Changed
L471-L485 (3.1.2 Primary	combined with the typically lower	combined with the typically lower	Changed

reactions of 2,4-DNP with O_3, •OH, and $•NO_2$)	atmospheric concentration of $•NO_2$ relative to •OH and O_3, the calculations might suggest that $•NO_2$ reactivity is negligible (Shi et al., 2025; Chapleski et al., 2016). However, to provide a complete picture, it is useful to distinguish three distinct levels of $•NO_2$ involvement in the atmospheric chemistry of 2,4-DNP, a distinction that has been emphasized in recent multiphase studies(Rana et al., 2023). Level (i) is the direct reaction of $•NO_2$ with the parent compound 2,4-DNP, which we have shown to be kinetically negligible even under nighttime conditions (see pseudo-first-order analysis below).	atmospheric concentration of $•NO_2$ relative to •OH and O_3, the calculations might suggest that $•NO_2$ reactivity is negligible(Shi et al., 2025; Chapleski et al., 2016). To distinguish the different roles of $•NO_2$ within the reaction framework examined here it is useful to distinguish three distinct levels of $•NO_2$ involvement in the atmospheric chemistry of 2,4-DNP, a distinction that has been emphasized in recent multiphase studies(Rana et al., 2023). Level (i) is the direct reaction of $•NO_2$ with the parent compound 2,4-DNP, which shows substantially lower calculated reactivity	

		than the •OH pathway under the concentration scenarios considered here.	
L492 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	while	although	Changed
L493 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	negligible	kinetically unfavorable in the investigated scenarios	Changed
L471-L485 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	may still be environmentally relevant. The possible involvement of •NO_2 in subsequent reactions with primary oxidation intermediates (Level ii) will be discussed separately in Section 3.1.3 to provide a complete mechanistic picture.	represent additional mechanisms within the pre-sent reaction framework. These pathways should not be considered a complete description of nighttime reactive-nitrogen chemistry because direct NO_3 oxidation was not included in the present calculations.	Changed

L509 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)		calculated	Added
L509 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	energy		Deleted
L510-L512 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	the disruptive effect of the solvent on the intramolecular cooperativity inherent to 2,4-DNP	changes in the balance between intramolecular and solute-solvent interactions upon solvation	Changed
L512 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	a strongly electron-donating	the	Changed
L513 (3.1.2 Primary reactions of 2,4-DNP with	strongly electron-withdrawing		Deleted

O_3, •OH, and •NO_2)			
L513-L514 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	groups induces a pronounced intramolecular electric field	substituents produces pronounced electronic polarization	Changed
L515-L516 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	geometry further enables stabilizing intramolecular hydrogen bonds	pattern enables intramolecular hydrogen bonding	Changed
L528-L546 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	For hydrogen abstraction reactions, the gas-phase pathway is associated with C–H bond dissociation energetics, where the C5–H bond is weakened by the adjacent nitro group and is therefore more susceptible to homolysis. In the aqueous phase, the calculated pathway exhibits increased proton-transfer character.	For the •OH HAA pathways, the preferred abstraction site also changes upon solvation. In the gas phase, abstraction from C5 is favored among the investigated HAA channels, whereas in the aqueous phase the hydroxyl hydrogen becomes more favorable in the calculated pathway. This change suggests that	Changed

	The hydroxyl hydrogen, due to its intrinsic acidity and the proton-transfer assistance provided by the hydrogen-bonding network of water, gains both kinetic and thermodynamic advantages, becoming the dominant abstraction site in solution.	solvation modifies the relative energetics of the competing H-abstraction sites, likely through differential stabilization of the reactant and transition-state structures. In contrast, the preferred HAA channel identified for •NO_2 involves abstraction from C6 in both phases, although this pathway remains kinetically unfavorable because of its high calculated barriers.	
L558 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	a characteristic		Deleted
L560-L563 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	which summarizes the thermodynamic and kinetic data for O3, •OH, and •NO2 in both gas and aqueous phases. Several trends are evident from	Among the reactions examined, the •OH pathway shows the highest calculated gas-phase rate coefficient,	Changed

	these data. The •OH pathway shows the highest kinetic activity,		
L565-L566 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	at 298.15 K, further confirming its role as the dominant atmospheric oxidant.		Deleted
L566-L568 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	notable activity in the aqueous phase, with a total aqueous-phase rate constant	a calculated aqueous-phase rate coefficient	Changed
L568-L570 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	highlighting the importance of aqueous environments in multiphase chemistry	indicating appreciable intrinsic reactivity in the aqueous phase	Changed
L570-L571 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	exhibits extremely low kinetic activity	is kinetically unfavorable	Changed
L571	total	calculated	Changed

(3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)			
L572 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	as low as	of	Changed
L573-L589 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	These values are more than 13 orders of magnitude lower than those of the •OH pathway. Even under conditions of elevated •NO_2 concentration, the contribution of this pathway to the transformation of 2,4-DNP is expected to be negligible. It should be emphasized that the trends described above, however, reflect only the intrinsic molecular reactivity of	These bimolecular rate coefficients describe the intrinsic reactivity of the investigated pathways and do not by themselves determine their relative importance in the atmosphere, which additionally depends on oxidant concentrations and phase partitioning. To examine whether the very low intrinsic reactivity of the direct •NO_2 pathway could be offset by nighttime •NO_2 accumulation,	Changed

	each oxidant; their actual atmospheric importance depends on oxidant concentrations, phase partitioning, and aerosol liquid water content. To bridge this gap between intrinsic reactivity and atmospheric relevance, pseudo-first-order rate constants were estimated using literature-reported oxidant concentrations. These estimates are presented below, providing a more realistic assessment of the relative contributions of each pathway under typical tropospheric conditions.	pseudo-first-order rate coefficients were estimated using literature-reported oxidant concentrations as illustrative scenarios.	
L591-L592 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	levels are lower due to rapid photolysis under daytime conditions	is rapidly photolyzed during daytime	Changed
L592 (3.1.2 Primary	During heavily	Under	Changed

reactions of 2,4-DNP with O_3, •OH, and •NO_2)			
L595 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)		molecules	Added
L595-L597 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	and in UK urban surface environments, night-time OH levels were determined to be in the range	while nighttime •OH concentrations	Changed
L597-L598 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)		have been reported in UK urban surface environments	Added
L598 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	Meanwhile	In contrast	Changed

L600 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)		as illustrative nighttime scenarios	Added
L601 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	under nighttime conditions can be estimated. For	for	Changed
L602 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)		is approximately 10^{-10} ~ 10^{-9} s^{-1}	Added
L602 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	with	based on	Changed
L603 (3.1.2 Primary reactions of 2,4-DNP with	and [OH] ≈ 10^5 ~ 10^6 molecules cm^{-3}, k'OH ≈ 10^{-10} ~ 10^{-9} s^{-1}		Deleted

O_3, •OH, and •NO_2)			
L604 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	with	a rate coefficient of	Changed
L605-L647 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	and [NO_2] ≈ 10^{10} ~ 10^{11} molecules cm^{-3} (corresponding to 0.4 ~ 4 ppb at 298 K and 1 atm), k'NO_2 ≈ 10^{-18} ~ 10^{-17} s^{-1}. Even under the most favorable nighttime conditions (lowest •OH, highest •NO_2), the direct •NO_2 pathway remains more than 7 orders of magnitude slower than the •OH pathway, corresponding to a lifetime of >10^{10} s, which is negligible on atmospheric timescales. Therefore, while a full diurnal box model	combined with a nighttime •NO_2 concentration of several ppb corresponds to a pseudo-first-order rate coefficient on the order of 10^{-17} s^{-1}. Thus, under the illustrative nighttime conditions considered here, the direct •NO_2 pathway remains more than seven orders of magnitude slower than the •OH pathway and is unlikely to compete effectively with •OH oxidation. Importantly, these estimates compare only the investigated	Changed

	simulation would be required to quantify all pathways under varying pollution regimes, the quantitative analysis above confirms that the direct reaction of •NO_2 with parent 2,4-DNP is negligible even under nighttime conditions. The possible involvement of •NO_2 in subsequent reactions with primary oxidation intermediates will be discussed separately to provide a complete mechanistic picture of its environmental fate. In summary, the atmospheric degradation of 2,4-DNP is kinetically dominated by •OH, with O_3 playing a significant role in the aqueous phase, while the direct transformation contribution of •NO_2	bimolecular reaction channels and should not be interpreted as the overall atmospheric lifetime of 2,4-DNP, which also depends on photolysis, deposition, phase partitioning, heterogeneous chemistry, and other loss processes. The aqueous-phase calculations additionally indicate appreciable intrinsic reactivity toward O_3. Accordingly, the relative contributions of the investigated pathways to the overall atmospheric loss of 2,4-DNP cannot be quantified without additional partitioning information and atmospheric chemical modeling. The possible involvement of •NO_2 in subsequent reactions	

	can be neglected in environmental assessments. The overall contribution of aqueous-phase reactions to the atmospheric fate of 2,4-DNP depends critically on the fraction of the compound that partitions into the aqueous phase. For 2,4-DNP, the Henry's law constant has been determined as 5.70 × 10^{-8} atm·m^3/mol at 5 °C(Lüttke and Levsen, 1997), indicating a strong tendency to partition into the aqueous phase. The partitioning is further modulated by its acid dissociation constant (pKa ≈ 4.09 at 25 °C), as the deprotonated phenolate form is substantially more water-soluble than	with primary oxidation intermediates is discussed separately below. The atmospheric contribution of aqueous-phase reactions additionally depends on the fraction of 2,4-DNP present in the aqueous phase. The Henry's law constant has been determined as 5.70 × 10^{-8} atm·m^3/mol at 5 °C(Lüttke and Levsen, 1997), while its acid dissociation constant (pKa ≈ 4.09 at 25 °C) further affects aqueous partitioning because the deprotonated form is more water-soluble than the neutral species (Schwarzenbach et al., 1988). In addition, the aerosol liquid water content also determines the aqueous volume	

	the neutral phenol(Schwarzenbach et al., 1988). In addition, the aerosol liquid water content—which varies widely depending on relative humidity, particle composition, and atmospheric conditions—determines the available aqueous volume for multiphase reactions.	available for multiphase reactions.	
L653-L654 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	constants are further validated through systematic benchmarking against	coefficients were further compared with	Changed
L659-L660 (3.1.2 Primary reactions of 2,4-DNP with O_3, •OH, and •NO_2)	clearly demonstrating the strong inhibitory	consistent with a strong deactivating	Changed
L676-L681 (3.1.2 Primary	Collectively, these results establish a robust and	Collectively, these comparisons support the	Changed

reactions of 2,4-DNP with O_3, •OH, and •NO_2)	quantitatively consistent framework for predicting the atmospheric oxidation kinetics of aromatic pollutants on the basis of their fundamental electronic structure.	qualitative role of electron-withdrawing nitro substituents in modulating the calculated reactivity of 2,4-DNP and related nitroaromatic compounds.	
L683-L684 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3')	As the primary initiator of atmospheric degradation of 2,4-DNP, •OH	Among the initiation pathways examined here, •OH addition	Changed
L686-L693 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3')	Reaction with molecular O_2 typically governs its rapid oxidative evolution, while its reaction with •NO_2 can lead to the formation of more toxic and more strongly light-absorbing nitrated products. Therefore, to fully delineate the atmospheric transformation pathways and final products of	The following calculations examine selected secondary reactions of IM3' with O_2 and •NO_2. These reactions were considered to evaluate the relative energetics of representative HAA and radical-addition pathways.	Changed

	2,4-DNP, it is essential to systematically investigate the reaction mechanisms of IM3' with both O_2 and $\bullet NO_2$.		
L701-L702 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3')	thermodynamics and kinetics	thermodynamically and kinetically	Changed
L714-L717 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3')	have much higher energy barriers and are therefore kinetically uncompetitive under realistic atmospheric conditions	have substantially higher calculated barriers and are therefore less favorable within the investigated reaction framework	Changed
L735 (3.1.3 The subsequent reactivity mechanism of the key intermediate		investigated IM3'+	Added

IM3’)			
L735 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3’)	is	has a	Changed
L735 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3’)	kinetically and		Deleted
L736 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3’)	more favorable	lower calculated barrier	Changed
L736 (3.1.3 The subsequent	path	pathway	Changed

reactivity mechanism of the key intermediate IM3')			
L737-L740 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3')	This establishes HAA as the dominant mechanism in the reaction of IM3' with •NO_2, consistent with the conclusion drawn for the O_2 system.	Thus, HAA is the lower-barrier pathway among the •NO_2 reaction channels examined here, consistent with the corresponding barrier comparison for the O_2 reaction system.	Changed
L742-L743 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3')	While O_2 dominates the overall fate of IM3' due to its concentration advantage (see below)	The calculated	Changed
L744-L748 (3.1.3 The subsequent reactivity mechanism of the key intermediate	suggests that nitration via this indirect route could be significant under elevated •NO_2 conditions, such as in polluted urban plumes at night	indicates that this indirect •NO_2 pathway is mechanistically feasible. However, its atmospheric contribution cannot be inferred from the energy barrier alone and depends	Changed

IM3’)		on competition with O_2 and other reactants	
L749-L752 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3’)	It should be emphasized that the competition between O_2 and $\bullet NO_2$ for IM3’ must be evaluated based on effective rates (k × [oxidant]) rather than second-order rate constants alone.	To illustrate this competition, effective pseudo-first-order rates (k × [oxidant]) were estimated using representative atmospheric concentrations and literature-based rate coefficients.	Changed
L754 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3’)		calculated	Added
L754-L754 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3’)	the barrier height indicates that the reaction is near the gas-kinetic limit, with		Deleted

L756 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3’)	alkyl	analogous	Changed
L756 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3’)		are	Added
L759 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3’)		an illustrative reaction timescale of approximately 0.2 μs	Added
L760 (3.1.3 The subsequent reactivity	a lifetime of 0.2 microseconds	. This estimate is	Changed

mechanism of the key intermediate IM3')			
L760-L761 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3')	well-established behavior that alkyl	generally rapid reactions of organic	Changed
L761 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3')	react		Deleted
L761-L762 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3')	on timescales of 10 ~ 100 nanoseconds		Deleted

L763-L765 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3')	even under the most favorable nighttime conditions with [•NO_2] ≈	assuming a representative nighttime •NO_2 concentration of	Changed
L765-L766 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3')	taking	a literature-based rate coefficient of	Changed
L767-L780 (3.1.3 The subsequent reactivity mechanism of the key intermediate IM3')	a lifetime of 1 ~ 10 seconds. Thus, k'O_2 is more than 6 orders of magnitude faster than k'NO_2. The overwhelming concentration advantage of O_2—more than 10^7 times that of •NO_2—ensures that the reaction of IM3' with O_2 is the dominant	an illustrative reaction timescale of approximately 0.2 μs. This estimate is consistent with the generally rapid reactions of organic radicals with O_2 (Vereecken and Francisco, 2012; Calvert et al., 2015). For the reaction of IM3'	Changed

	atmospheric fate of this intermediate. This is fully consistent with the established behavior that addition of O_2 is essentially the sole atmospheric fate of organic radicals formed during the oxidation of organic compounds(Calvert et al., 2015).	with $\bullet NO_2$ via HAA (barrier = 2.01 kcal mol^{-1}), assuming a representative nighttime $\bullet NO_2$ concentration of $10^{10} \sim 10^{11}$ molecules cm^{-3} and a literature-based rate coefficient of $k NO_2 \approx 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} gives $k' NO_2 \approx 10^{-1} \sim 1$ s^{-1}, corresponding to an illustrative reaction timescale of approximately 1 ~ 10 s. Under these assumptions, the effective O_2 reaction rate exceeds that of the investigated $\bullet NO_2$ pathway by more than six orders of magnitude. Thus, although the low calculated barrier demonstrates the mechanistic feasibility of the indirect $\bullet NO_2$ pathway, the illustrative effective-rate	

		comparison suggests that reaction with O_2 would strongly outcompete the investigated $\bullet NO_2$ pathway under the conditions considered here. Quantifying the atmospheric branching of IM3' would require reaction-specific rate coefficients and a more complete treatment of competing loss processes.	
L784-L785 (3.2. Molecular dynamics)	As a representative model of atmospheric nanoparticles,		Deleted
L785 (3.2. Molecular dynamics)	offers an ideal system	provides a well-defined model system	Changed
L892 (3.2. Molecular dynamics)	can		Deleted
L892 (3.2. Molecular dynamics)	substantially		Deleted
L893-L909	they collectively	and influence the	Changed

(3.2. Molecular dynamics)	determine the physical state and water uptake of aerosol particles. Their absence in the current model means that the simulated hydration effects represent a simplified scenario that may not fully capture the complexity of real aerosol surfaces. Consequently, the MD results should be interpreted as molecular-scale insights into adsorption behavior under idealized conditions, rather than as direct predictions of atmospheric persistence or humidity-dependent partitioning. Quantitative assessments of atmospheric residence time, gas–particle partitioning, or	physical state and water uptake of aerosol particles. The simulated hydration effects therefore represent a simplified model system. The MD results should be interpreted as molecular-scale insights into adsorption behavior rather than as direct predictions of atmospheric persistence or humidity-dependent partitioning. The present simulations do not quantitatively constrain atmospheric residence time, gas-particle partitioning, or long-range transport. These quantities require additional partitioning calculations and atmospheric chemical and transport modeling.	

	long-range transport would require additional modeling that incorporates these aerosol properties and atmospheric transport processes, and are beyond the scope of the present study.		
L910 (3.3. Predicted toxicity indicators)	Ecotoxicity assessment	Predicted toxicity indicators	Changed
L914 (3.3. Predicted toxicity indicators)	, one of the key atmospheric oxidants	pathway	Changed
L915-L917 (3.3. Predicted toxicity indicators)	enables a precise analysis of the oxidation degradation pathways of 2,4-DNP and the toxicity of its products.	provides a defined reaction set for examining predicted changes in toxicity indicators among selected transformation products	Changed
L922-L923 (3.3. Predicted toxicity indicators)	aiming to reveal the toxicity evolution pattern	examine changes in predicted toxicity indicators	Changed
L924	mass-fate		Deleted

(3.3. Predicted toxicity indicators)			
L924-L925 (3.3. Predicted toxicity indicators)	DFT kinetics	investigated DFT reaction pathways	Changed
L925-L926 (3.3. Predicted toxicity indicators)	adsorption	-derived interfacial adsorption behavior	Changed
L926-L928 (3.3. Predicted toxicity indicators)	illustrate the overall atmospheric transformation framework of 2,4-DNP	summarize the scope of the present computational framework	Changed
L933-L935 (3.3. Predicted toxicity indicators)	of transformation products are evaluated via yield-weighted QSAR prediction	indicators of selected transformation products were evaluated using QSAR models	Changed
L939 (3.3. Predicted toxicity indicators)	The risk differences in	Differences in the predicted	Changed
L940 (3.3. Predicted toxicity indicators)	potential	indicators	Changed
L943-L944	within the safety	below the model	Changed

(3.3. Predicted toxicity indicators)		classification	
L945-L980 (3.3. Predicted toxicity indicators)	its ozonolysis products display a marked divergence in mutagenic potential. Although primary intermediates (IM17, IM25, IM44, IM54) show no detectable mutagenicity, the final products generally demonstrate elevated mutagenic risk. Notably, the predicted value for product P1 (0.53) exceeds the toxicity threshold, placing it within the high-risk zone. This result clearly indicates that the ozonolysis does not necessarily reduce the mutagenicity of 2,4-DNP, instead, by generating more reactive intermediates	the final products show higher predicted Ames mutagenicity indicators in the QSAR model. Notably, the predicted value for P1 (0.53) exceeds the model classification threshold. Within the QSAR framework, these results indicate that ozonolysis does not uniformly decrease the predicted Ames mutagenicity indicators of the modeled products. For developmental toxicity (Figure 7b), the parent compound has a predicted value of 0.55, whereas the modeled ozonolysis products generally show higher predicted values, with	Changed

	and final products, it may significantly increase the overall genotoxic risk of the reaction system. In terms of developmental toxicity in Figure 7b, 2,4-DNP itself shows a baseline potential of 0.55, which is further exacerbated by ozonolysis. All derived products show higher developmental toxicity than the parent compound, with the risk reaching a maximum for IM54 (0.94). Notably, P2 and P4, despite their relatively low Ames mutagenicity (0.21), still exhibit a developmental toxicity potential of 0.56, which are higher than that of the parent compound. This reveals a decoupling between mutagenicity and	IM54 reaching 0.94. P2 and P4 have predicted values of 0.56, slightly higher than that of the parent compound. The differences between the Ames mutagenicity and developmental toxicity predictions further illustrate that the two QSAR endpoints do not necessarily vary in parallel across the modeled transformation products. Overall, the QSAR analysis predicts that some ozonolysis products have higher Ames mutagenicity and/or developmental toxicity indicators than the parent 2,4-DNP. These compound-level predictions describe changes in modeled toxicity indicators and should not be interpreted as demonstrating	

	developmental toxicity, suggesting that the oxidation process may generate novel hazardous specific developmental toxicity even when their mutagenic potential remains relatively low. Overall, the analysis indicates that the ozonolysis of 2,4-DNP does not constitute a harmless degradation pathway. On the contrary, it leads to the generation of more intermediate and final products with enhanced mutagenic and developmental toxicity.	increased environmental or health risk, which would additionally require information on product yields, environmental concentrations, exposure, and experimentally validated toxicity.	
L1019-L1021 (3.3. Predicted toxicity indicators)	—is recommended for the high-priority compounds identified here.	would be valuable for evaluating the QSAR-predicted toxicity indicators of selected transformation products.	Changed
L1023-L1025 (4 Conclusions)	the chemical transformation	selected chemical transformation pathways,	Changed

	mechanisms, multiphase interfacial behavior, and toxicity evolution	molecular-scale interfacial behavior, and predicted toxicity changes	
L1026 (4 Conclusions)	in the atmosphere		Deleted
L1027-L1032 (4 Conclusions)	The main quantitative findings are: the atmospheric degradation of 2,4-DNP is dominated by the •OH pathway in the gas phase, whileO_3 plays a significant role in the aqueous phase	Among the direct gas-phase reactions examined here, the calculated rate coefficient for the •OH pathway is higher than those for O_3 and •NO_2, while the aqueous-phase calculations indicate appreciable intrinsic reactivity toward O_3	Changed
L1033 (4 Conclusions)	~	on the order of	Changed
L1034 (4 Conclusions)	, more than 13 orders of magnitude lower than that of •OH		Deleted
L1036-L1037 (4 Conclusions)	distinct pathways that may be environmentally relevant under certain conditions	additional mechanistic pathways that warrant further investigation	Changed
L1038-L1039 (4 Conclusions)	suppress the initial reaction rates	substantially affect the calculated reaction	Changed

		kinetics	
L1039-L1051 (4 Conclusions)	the key radical intermediate from •OH addition reacts with O_2 and •NO_2 predominantly via HAA; MD simulations reveal that the adsorption behavior of 2,4-DNP on the idealized C60 aerosol surogate is regulated non-monotonically by the degree of interfacial hydration, with enhanced solute-particle interactions under low-hydration conditions and weakened adsorption under high-hydration conditions	within the investigated O_2 and •NO_2 reaction systems, HAA exhibits the lowest calculated barrier among the examined secondary pathways; MD simulations show a non-monotonic hydration dependence of 2,4-DNP adsorption in the idealized C60/water system, with changes in hydration altering the molecular adsorption configurations and interaction strengths. These MD results represent molecular-scale behavior within the idealized model system and do not provide quantitative constraints on atmospheric residence time,	Changed

		gas-particle partitioning, or long-range transport;	
L1052 (4 Conclusions)	elevated	higher predicted	Changed
L1053 (4 Conclusions)	relative to	than	Changed
L1053-L1061 (4 Conclusions)	Compared to previous studies that focused on gas-phase photolysis and assumed oxidative detoxification, our work quantifies the cumulative electron-withdrawing effect of two nitro groups (rate constant three orders lower than mononitrocatechol) and predicts that ozonolysis products may exhibit increased toxicity indicators, challenging conventional assumptions that oxidative degradation necessarily leads to detoxification.	These results represent compound-level, screening-level predictions and do not establish increased environmental risk, which would require information on product yields, exposure, and experimentally validated toxicity.	Changed

L1061-L1063 (4 Conclusions)	qualitative framework established here—linking	mechanistic relationships examined here among	Changed
L1063 (4 Conclusions)	, to		Deleted
L1063 (4 Conclusions)		predicted	Added
L1064-L1066 (4 Conclusions)	serve as a reference for understanding related nitroaromatic systems.	provide a basis for future investigations of related nitroaromatic compounds.	Changed
L1067 (4 Conclusions)	the	The	Changed
L1069 (4 Conclusions)	—particularly the presence of	including	Changed
L1071-L1088 (4 Conclusions)	As a result, the C60 model may overestimate the contribution of π-π interactions and underestimate the role of polar interactions. The 1 ns MD timescale is sufficient for the rigid C60/small molecule system studied here, but longer simulations and polarizable force fields may be needed to capture slower	Consequently, the present model may emphasize π-π interactions while underrepresenting polar and chemically heterogeneous surface interactions. The present 1 ns MD simulations are limited in their ability to capture slower dynamical processes, particularly those occurring on more	Changed

	dynamical processes on more complex surfaces. The QSAR toxicity predictions are screening-level estimates requiring experimental validation. A full diurnal box model simulation incorporating temporally resolved oxidant concentrations, Henry's law partitioning, and aerosol liquid water content would be needed to fully quantify the atmospheric importance of each pathway under realistic conditions.	complex aerosol surfaces; longer simulations and more advanced force-fields treatments would therefore be valuable in future studies. The QSAR toxicity predictions are screening-level estimates requiring experimental validation. Moreover, quantitative determination of the relative contributions of the investigated pathways to the atmospheric loss of 2,4-DNP would require atmospheric chemical modeling that incorporates temporally resolved oxidant concentrations, gas-particle and gas-aqueous partitioning, aerosol liquid water content, and additional loss	

		processes.	
L1092-L1117 (4 Conclusions)	Based on these findings, we recommend the following directions for future research: (i) Experimental validation of predicted kinetics: Advanced kinetic techniques such as laser-induced fluorescence or cavity ring-down spectroscopy should be employed to measure the rate constants for the reactions of 2,4-DNP with O_3 and •OH, providing direct experimental confirmation of the theoretical trends. (ii) In vitro toxicity testing: The high-priority ozonolysis products identified in this study (IM54, P1, and P2) should be subjected to	Future work should therefore focus on experimental validation of the calculated reaction kinetics and QSAR predictions, more realistic representations of carbonaceous aerosol surfaces, and atmospheric chemical modeling that explicitly incorporates phase partitioning and relevant loss processes. Within these limitations, the present results provide molecular-level mechanistic information that can guide future experimental and modeling studies of nitrophenol multiphase chemistry.	Changed

	Ames mutagenicity assays and zebrafish embryo developmental toxicity tests to validate the QSAR predictions. (iii) Refined interfacial models: Complementary MD simulations using more realistic carbonaceous models, such as functionalized graphene or amorphous carbon clusters, would help assess the influence of surface functional groups and defects on the adsorption behavior of 2,4-DNP. (iv) Diurnal box model simulations: Full diurnal chemical box models incorporating temporally resolved oxidant concentrations, Henry's law partitioning, and aerosol liquid water content are needed to		

	fully quantify the atmospheric importance of each oxidation pathway under different pollution regimes. Despite these caveats, the mechanistic insights into the molecular-level reactivity and interfacial behavior of 2,4-DNP provide a foundation for future experimental and modeling studies on the multiphase fate of nitrophenolic compounds.		
L1348-L1353 (References)		Rana, M. S. and Guzman, M. I.: Mechanistic Insights into Heterogeneous Oxidation: Product-Resolved Analysis of Phenolic Aldehyde Films, ACS Physical Chemistry Au, 2026a. Rana, M. S. and	Added

		Guzman, M. I.: Heterogeneous Nitrate Radical Oxidation of Catechol Produces Nitrocatechols, Oligomers, and Brown Carbon, ACS Earth & Space Chemistry, 10, 2159 - 2170, 2026b.	