Supplement of Atmos. Chem. Phys., 26, 15563–15582, 2026
https://doi.org/10.5194/acp-26-15563-2026-supplement
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Atmospheric Chemistry and Physics Open Access

Supplement of

Unveiling the multiphase fate of 2,4-dinitrophenol on aerosols: interfacial hydration modulates competing oxidation pathways and predicted toxicity indicators

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Table S1 The reaction energies ($\Delta_r E$) of 2,4-DNP + •OH→IM3 at various levels of theory. Units of is kcal mol^{-1}.

Methods	$\Delta_r E$(kcal mol^{-1})	Note
CCSD(T)/6-31+g(d,p)	-17.11	
M062x/6-311++g(3df,2p)	-18.28	ZPEs from
M062X/def2-TZVP	-18.73	M06-2X/6-31+g(d,p)
M062X/aug-cc-pVDZ	-19.50	

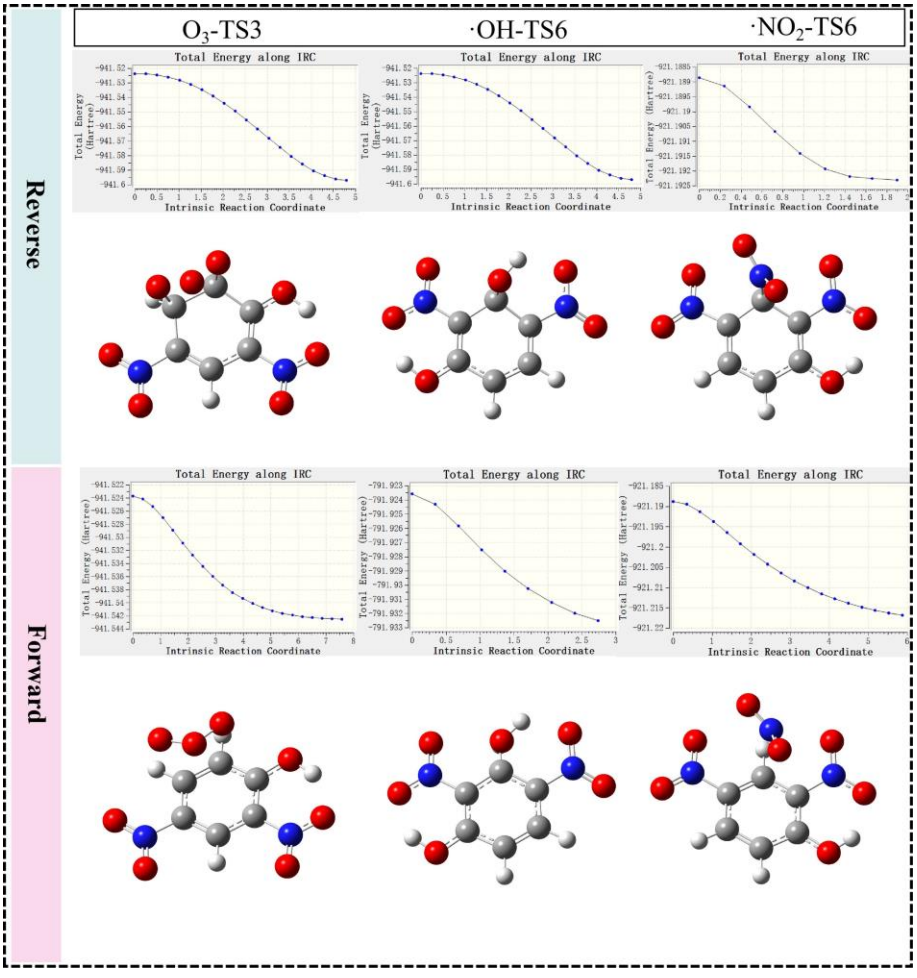


Figure S1 The IRC analysis of important transition states.

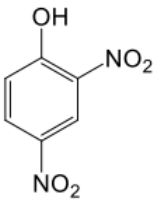
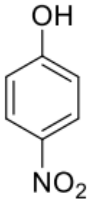
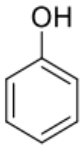
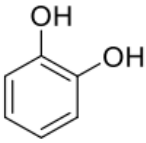
Table S2 Optimized bond lengths (Å) of the stationary points along the O_3, •OH, •NO_2 and IM3' reaction pathways of 2,4-DNP.

Reaction	Species	Key Bonds	Value (Å)	Description
O_3 Addition	TS6	C5–O1 (forming)	1.43	O_3 terminal oxygen approaches C5
		C6–O3 (forming)	1.42	O_3 terminal oxygen approaches C6
		C5–C6	1.38 → 1.56	Elongation of double bond
		O2–O3 (breaking)	2.02	O–O bond cleavage
	TS6-17	C5–C6	1.96	Further elongation
		C5–O1 (forming)	1.32	New C–O bond formation
		C6–O3 (forming)	1.26	New C–O bond formation
•OH Addition	TS3'	O•OH–C3 (forming)	1.42	•OH oxygen approaches C3
		C2–C3	1.40 → 1.50	Local aromatic disruption
		C3–C4	1.40 → 1.50	Local aromatic disruption
•OH HAA	TS9'	O•OH–H (C5) (forming)	1.19	•OH oxygen approaches C5–H
		C5–H (breaking)	1.08 → 1.26	C–H bond cleavage
•NO_2 HAA	TS7*	O–H (breaking)	0.98 → 1.21	Hydroxyl H abstraction
		H–ONO (forming)	1.08 → 0.97	New H–ONO bond formation
IM3' + O_2 HAA	TSB	Oa (O_2)–H (forming)	~1.17	O_2 approaches C3–H
		C3–H (breaking)	~1.30	C–H bond cleavage

Table S3 The total rate constants (cm^3 $molecule^{-1}$ s^{-1}) of 2,4-DNP with O_3, •OH, $•NO_2$ in the gas phase and aqueous phase

T(K)	Phase	k-O_3	k-•OH	k-$•NO_2$
200		1.78×10^{-26}	2.87×10^{-16}	5.37×10^{-35}
225		2.36×10^{-25}	6.13×10^{-16}	8.12×10^{-33}
250		1.92×10^{-24}	1.16×10^{-15}	4.65×10^{-31}
275		1.09×10^{-23}	2.02×10^{-15}	1.31×10^{-29}
300	Gas	4.72×10^{-23}	3.30×10^{-15}	2.16×10^{-28}
325		1.66×10^{-22}	5.10×10^{-15}	2.36×10^{-27}
350		4.97×10^{-22}	7.55×10^{-15}	1.87×10^{-26}
375		1.30×10^{-21}	1.08×10^{-14}	1.14×10^{-25}
400		3.07×10^{-21}	1.50×10^{-14}	5.63×10^{-25}
200		1.38×10^{-21}	6.26×10^{-22}	6.99×10^{-38}
225		4.02×10^{-20}	2.09×10^{-20}	1.34×10^{-34}
250		6.05×10^{-19}	3.54×10^{-19}	5.76×10^{-32}
275		5.63×10^{-18}	3.65×10^{-18}	8.35×10^{-30}
300	Aqueous	3.65×10^{-17}	2.60×10^{-17}	5.35×10^{-28}
325		1.79×10^{-16}	1.39×10^{-16}	1.82×10^{-26}
350		7.05×10^{-16}	5.90×10^{-16}	3.79×10^{-25}
375		2.33×10^{-15}	2.09×10^{-15}	5.31×10^{-24}
400		6.70×10^{-15}	6.39×10^{-15}	5.38×10^{-23}

Table S4 The experimental rate constant (cm^3 $molecule^{-1}$ s^{-1}) values of various phenols with •OH in the gas phase.

Compound	Structure formula	Rate constants
2,4-DNP		2.91×10^{-12}
Nitrophenol		1.99×10^{-11}
Phenol		2.30×10^{-11}
Catechol		1.04×10^{-10}

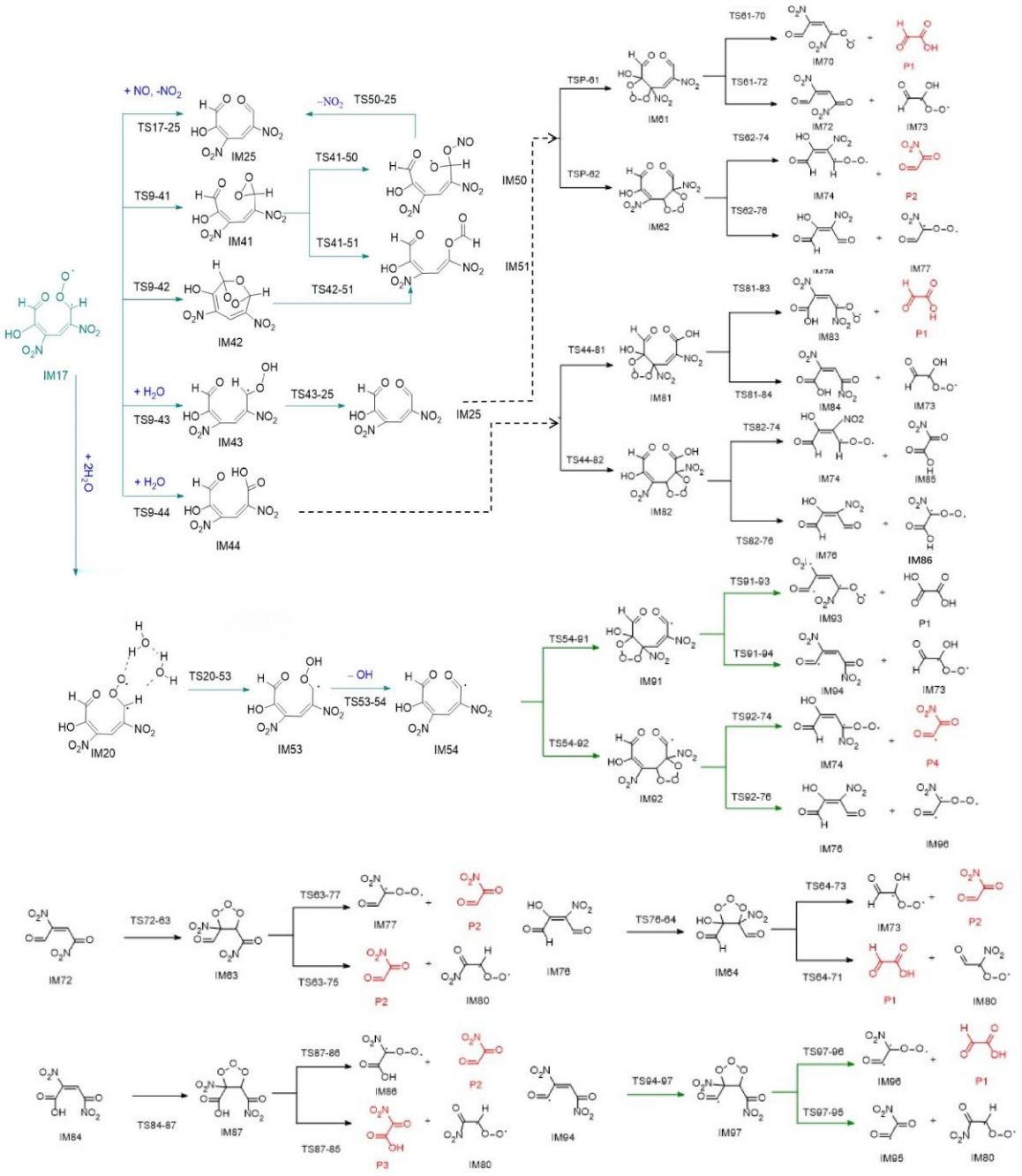


Figure S2 The subsequent reaction of the intermediate IM1.

Table S5 Cross-validation of Ames mutagenicity, development toxicity for 2,4-DNP and the intermediates (IMs series) and final products (Ps series) using T.E.S.T. and Toxtree. "ND" = not detected (negative), "D" = detected (positive), "NA" = not applicable/outside applicability domain. Cramer Class III indicates the highest priority for toxicity concern.

Compound	T.E.S.T. Ames muagenicity	Toxtree Ames muagenicity	T.E.S.T. Dev. Tox.	Toxtree Cramer Class
2,4-DNP	ND (0.13)	ND	D (0.55)	III
IM17	NA (0)	ND	D (0.67)	III
IM25	NA (0)	ND	D (0.85)	III
IM44	NA (0)	ND	D (0.84)	III
IM54	NA (0)	ND	D (0.94)	III
P1	D (0.53)	ND	D (0.58)	III
P2	ND (0.21)	D	D (0.56)	III
P3	ND (0.47)	ND	D (0.65)	III
P4	ND (0.21)	ND	D (0.56)	III

Note: Ames mutagenicity negative: Ames mutagenicity ≤ 0.50, Ames mutagenicity positive: Ames mutagenicity > 0.50. Development non-toxicant: developmental toxicity < 0.50, development toxicant: development toxicity > 0.50.

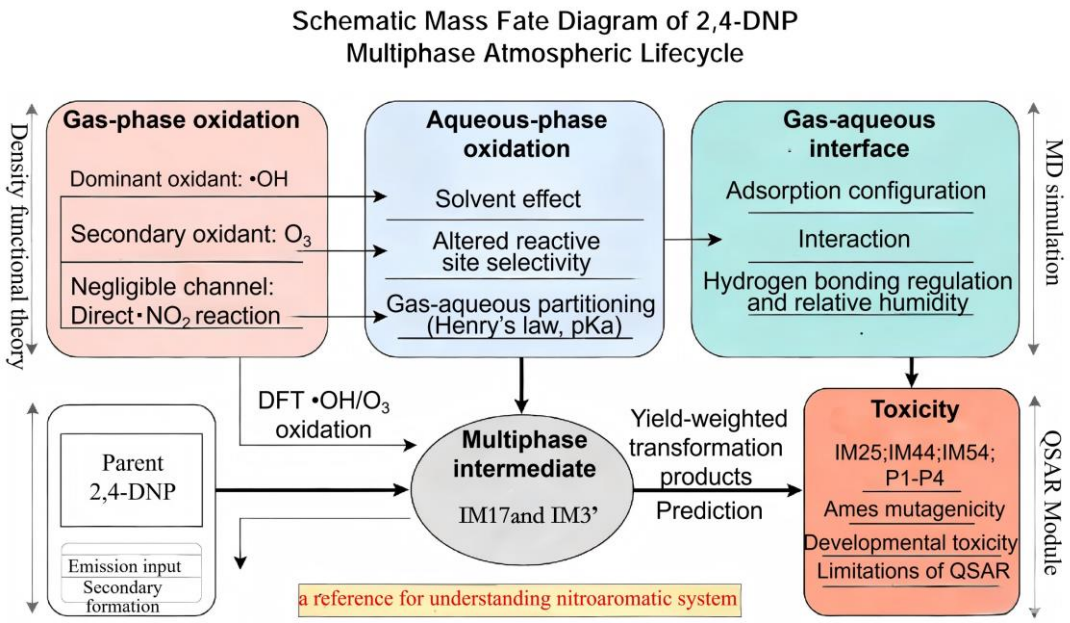


Figure S3 Conceptual mass-fate diagram of 2,4-DNP in the atmosphere, integrating DFT kinetics, MD adsorption, and QSAR toxicity predictions. The diagram illustrates gas-aqueous partitioning, parallel transformation pathways (gas-phase oxidation, aqueous-phase oxidation, and heterogeneous reactions), and the toxicity evaluation of transformation products.