Supporting information (SI)

Amine Ozonation Products Promote Sulfate Formation and Accelerate New Particle Growth

Weina Zhang[1,2], Jiale Lao[1,2], Yao Zhou[1,2], Ruijing Li[1,2], Shangyu Zhu[1,2], Guiying Li[1,2], Yuemeng Ji[1,2], Taicheng An[1,2,*]

[1] Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, Guangdong-Hong Kong-Macao Joint Laboratory for Contaminants Exposure and Health, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou, 510006, China.

[2] Guangdong Basic Research Center of Excellence for Ecological Security and Green Development, Key Laboratory for City Cluster Environmental Safety and Green Development of the Ministry of Education, School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou, 510006, China.

* Corresponding author: Prof. Taicheng An, E-mail: antc99@gdut.edu.cn

This SI includes a total of 12 pages (including this page) with 20 Figures and 3 Tables.

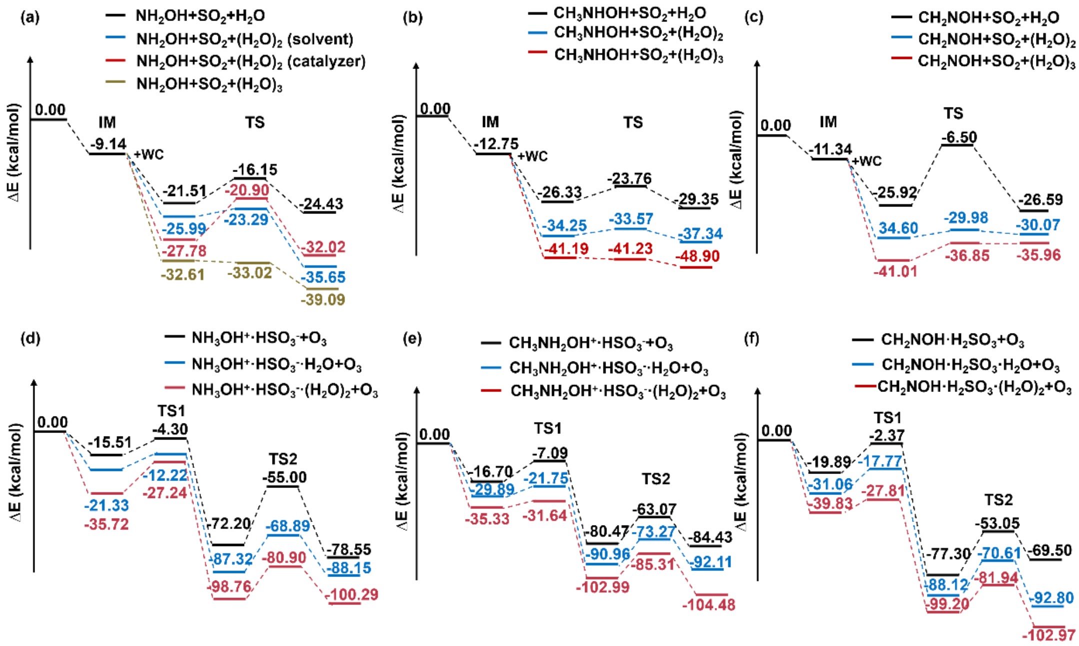

Figure S1. Potential energy surfaces of hydrolysis and ozonation reactions of three OH-amines with 1 ~ 3 water molecules.

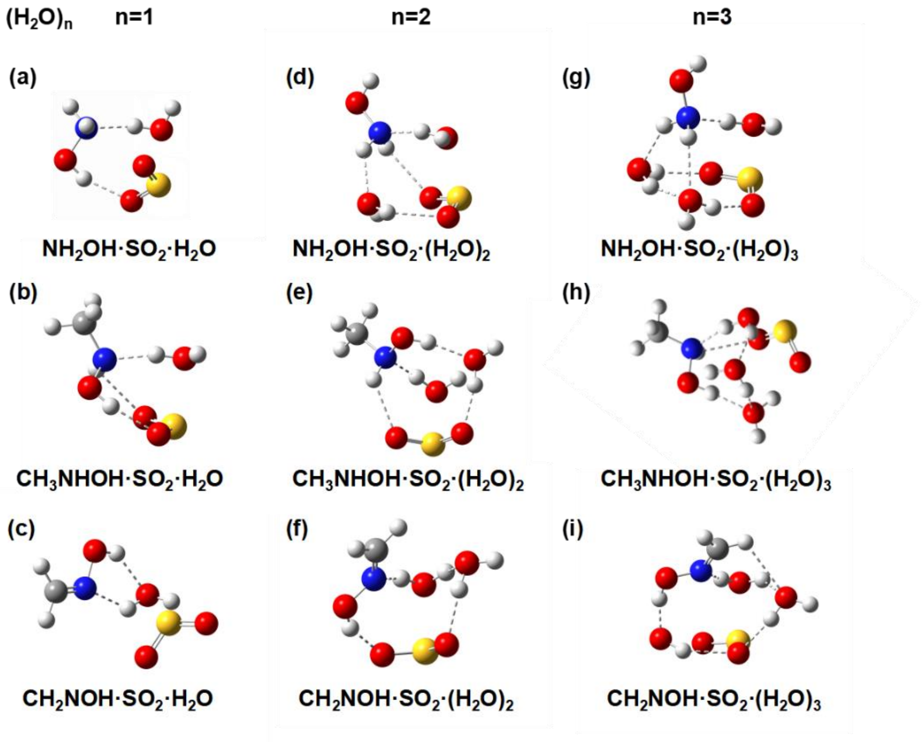

Figure S2. Structures of hydrolysis reaction reactant clusters (C1) including OH-amines.

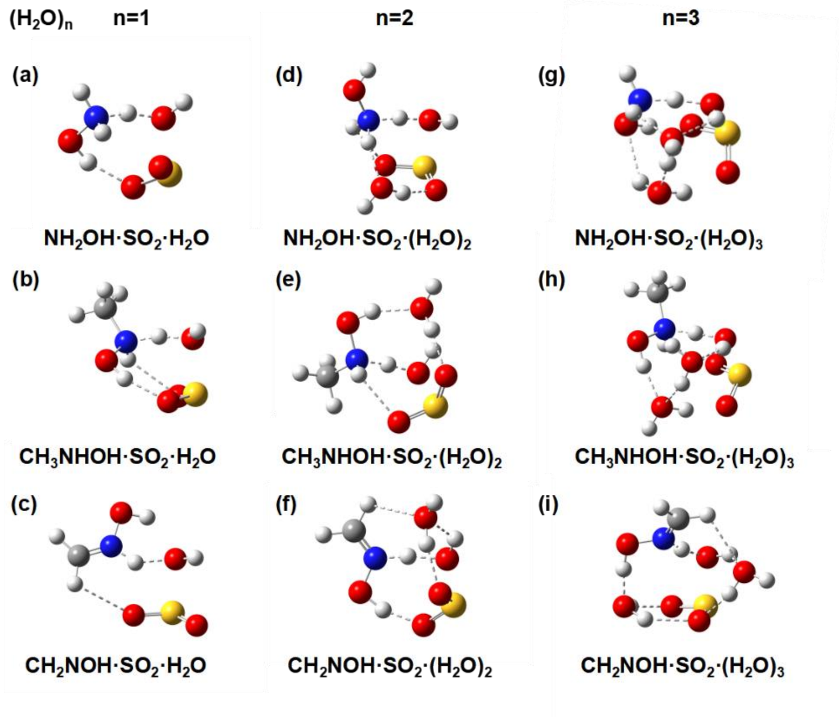

Figure S3. Structures of hydrolysis reaction transition state clusters (TS1) including OH-amines.

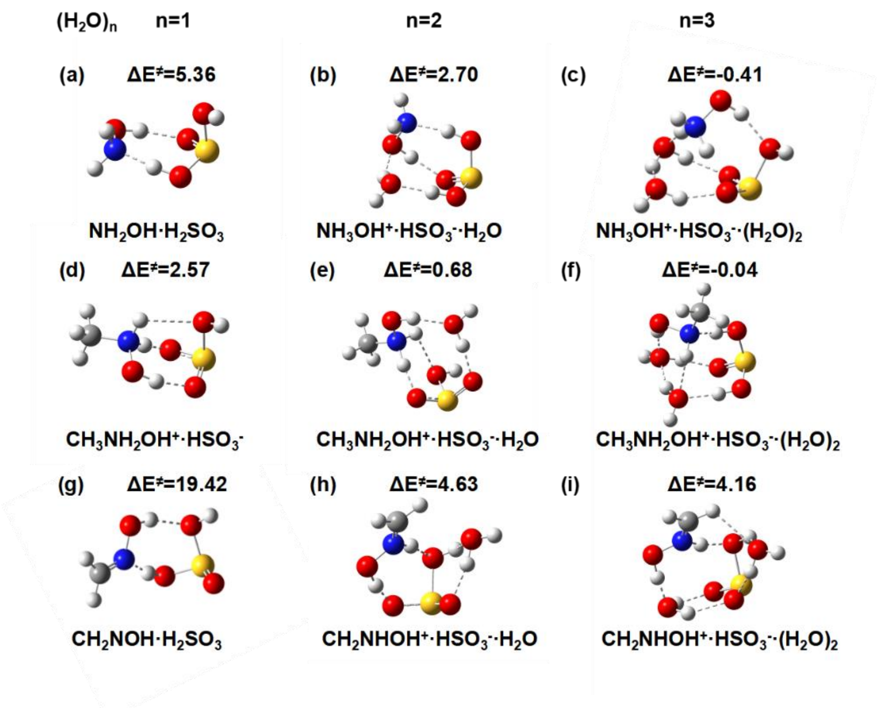

Figure S4. Structures of hydrolysis reaction product clusters (P1) including OH-amines ($\Delta E^{\neq}$, in kcal/mol).

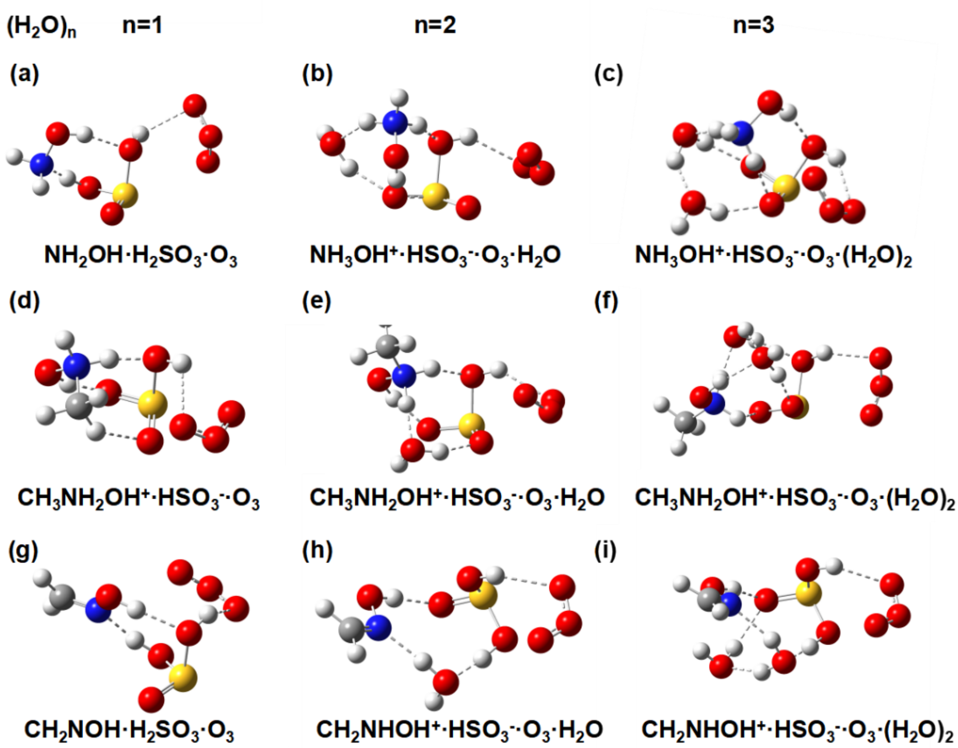

Figure S5. Structures of ozonation reaction reactant clusters (P2) including OH-amines.

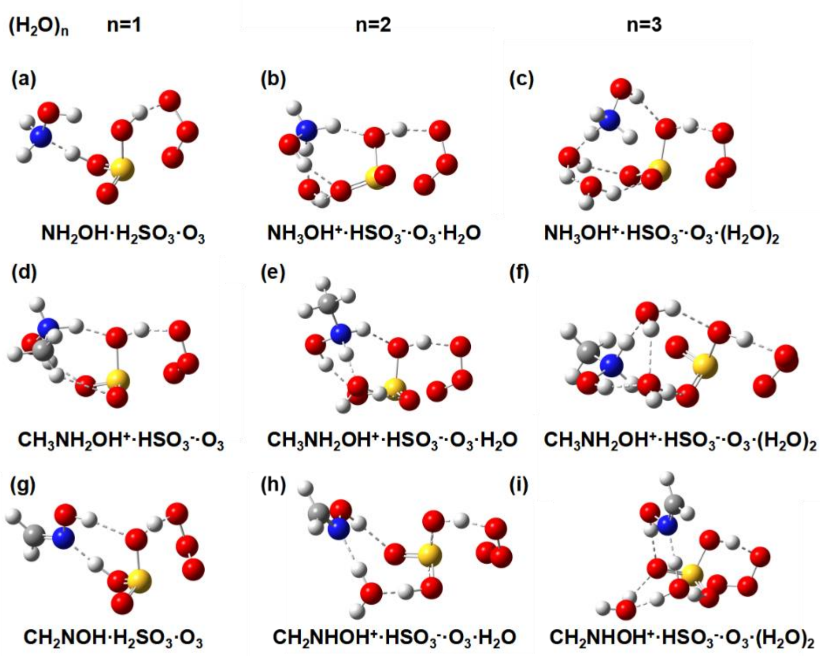

Figure S6. Structures of ozonation reaction transition state clusters (TS2) including OH-amines.

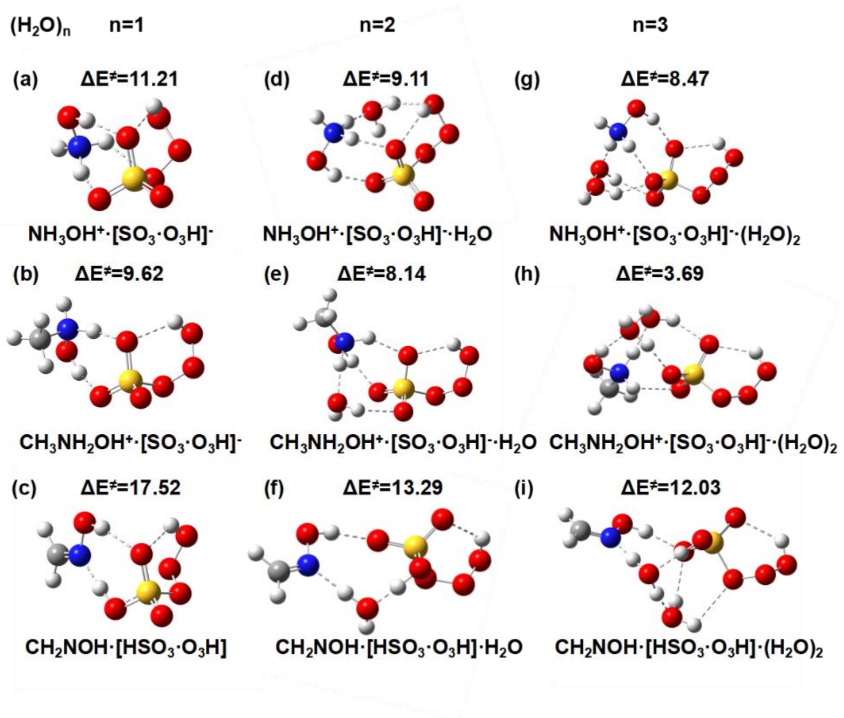

Figure S7. Structures of ozonation reaction product clusters (P3) including OH-amines ($\Delta E^{\neq}$, in kcal/mol).

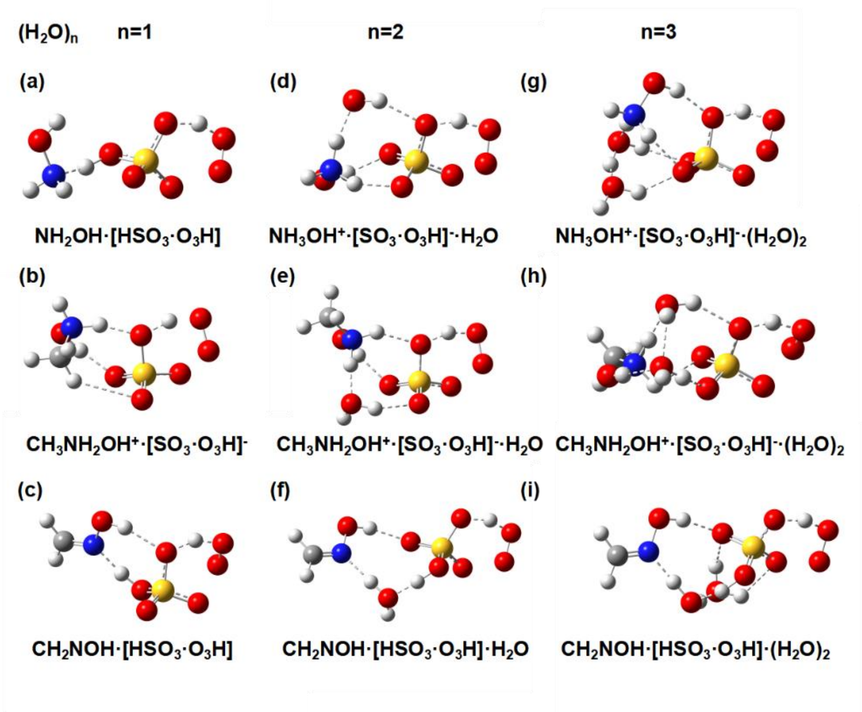

Figure S8. Structures of ozonation reaction transition state clusters (TS3) including OH-amines.

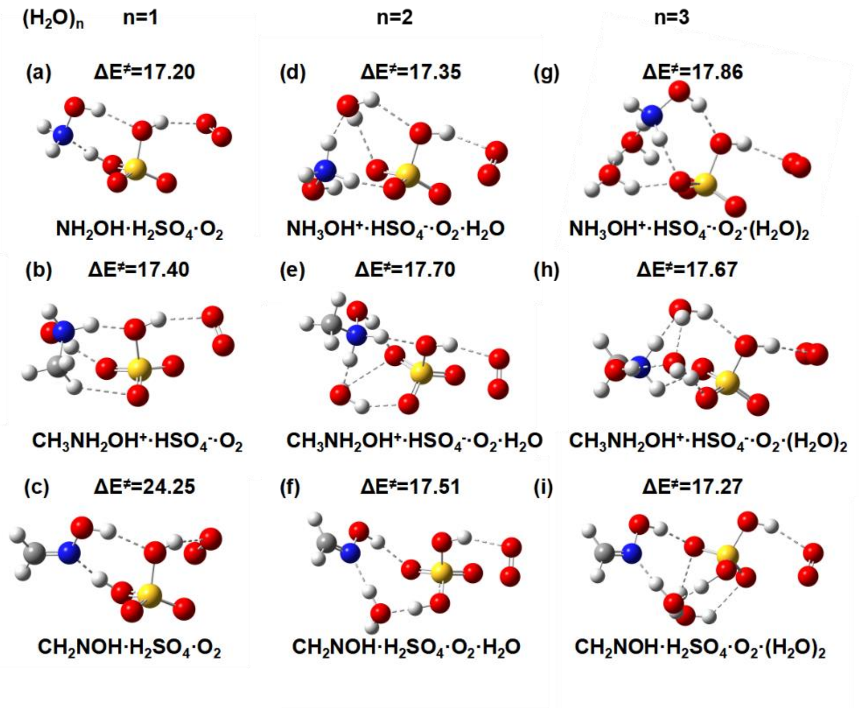

Figure S9. Structures of ozonation reaction product clusters (P4) including OH-amines ($\Delta E^{\neq}$, in kcal/mol).

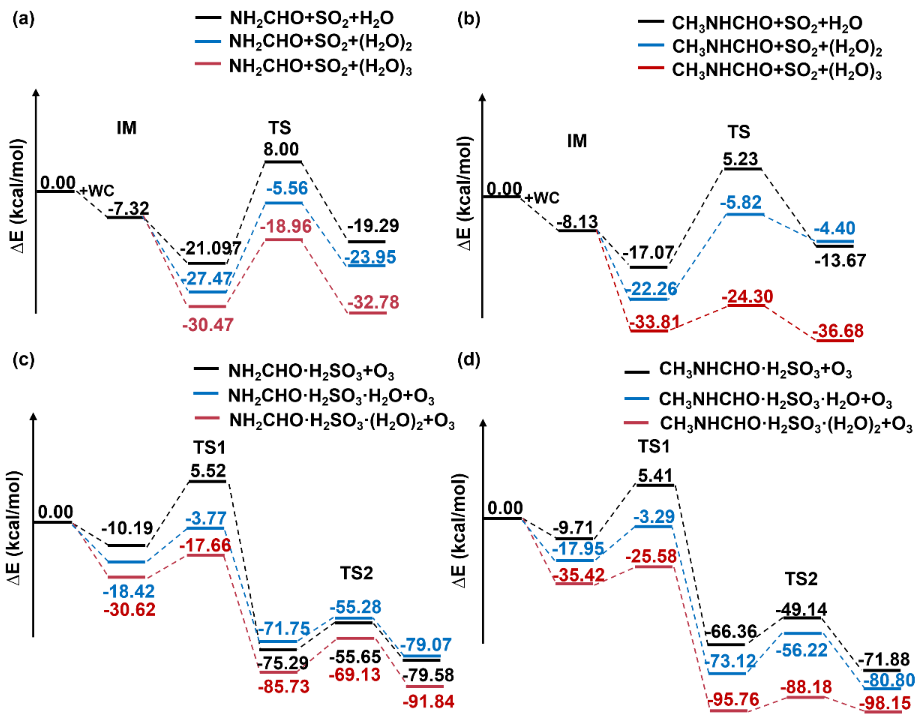

Figure S10. Potential energy surfaces of hydrolysis and ozonation reactions of three CHO-amines with 1 ~ 3 water molecules.

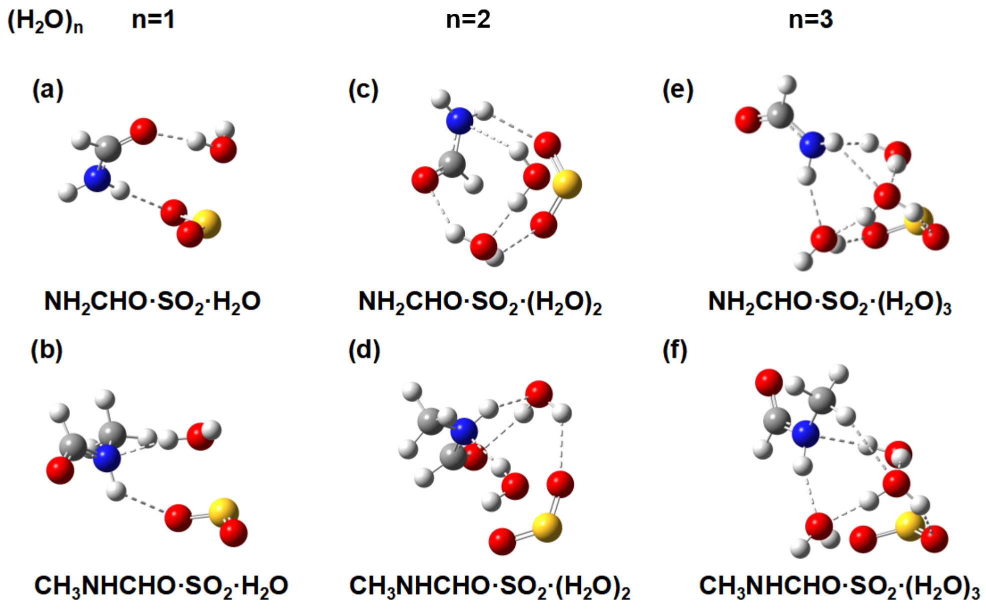

Figure S11. Structures of hydrolysis reaction reactant clusters (C1) including CHO-amines.

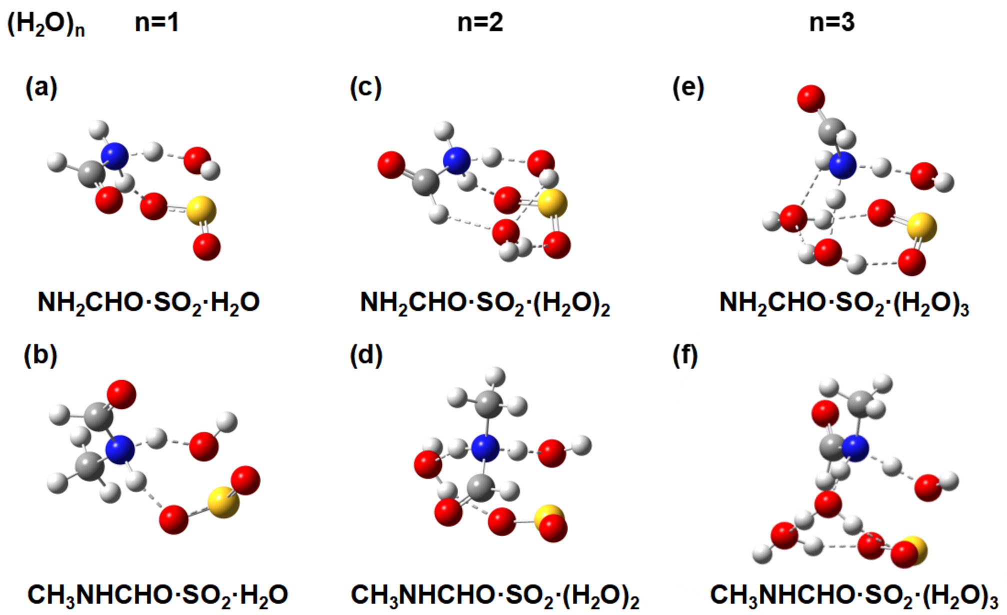

Figure S12. Structures of hydrolysis reaction transition state clusters (TS1) including CHO-amines.

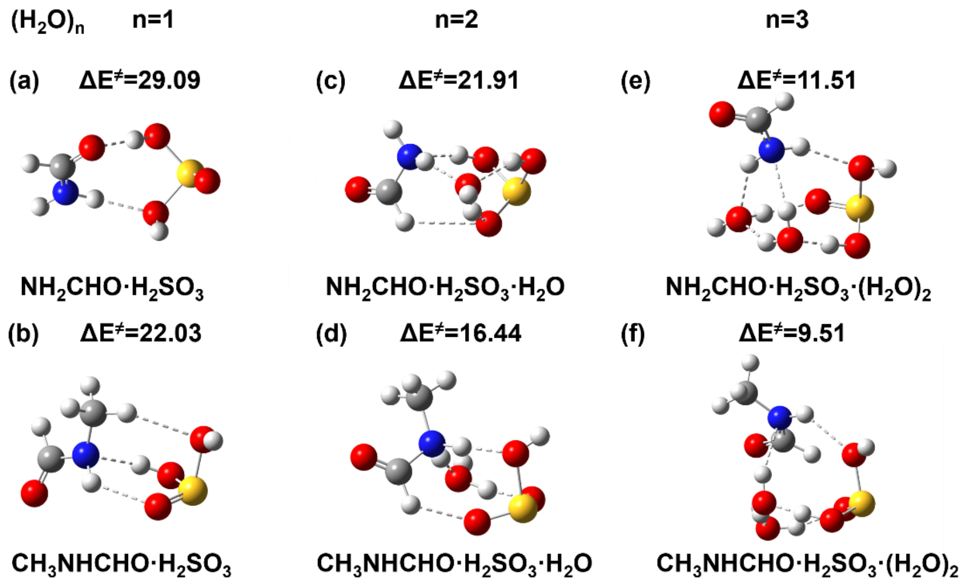

Figure S13. Structures of hydrolysis reaction product clusters (P1) including CHO-amines ($\Delta E^{\neq}$, in kcal/mol).

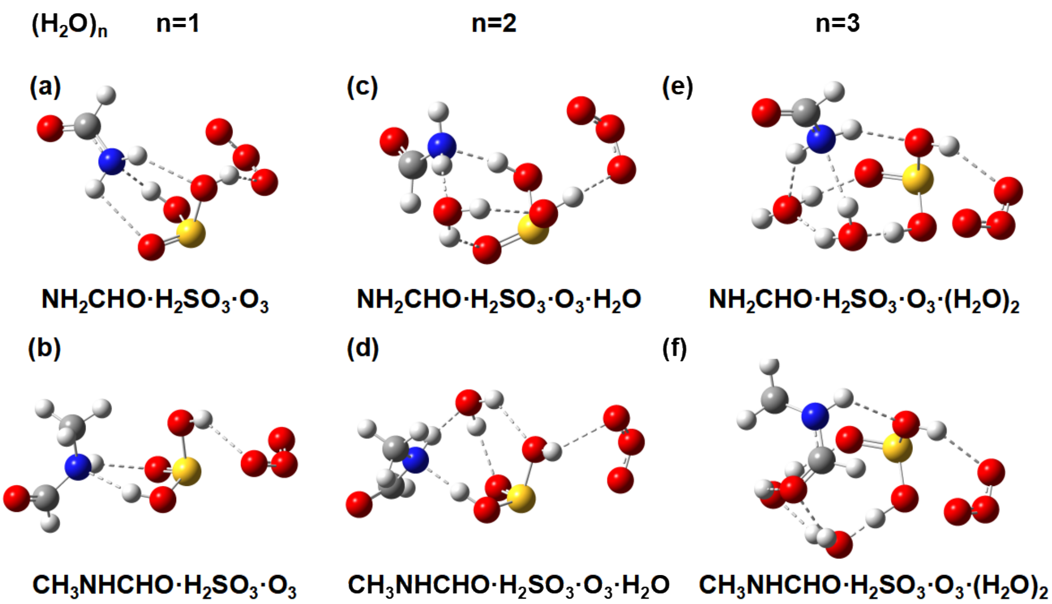

Figure S14. Structures of ozonation reaction reactant clusters (P2) including CHO-amines.

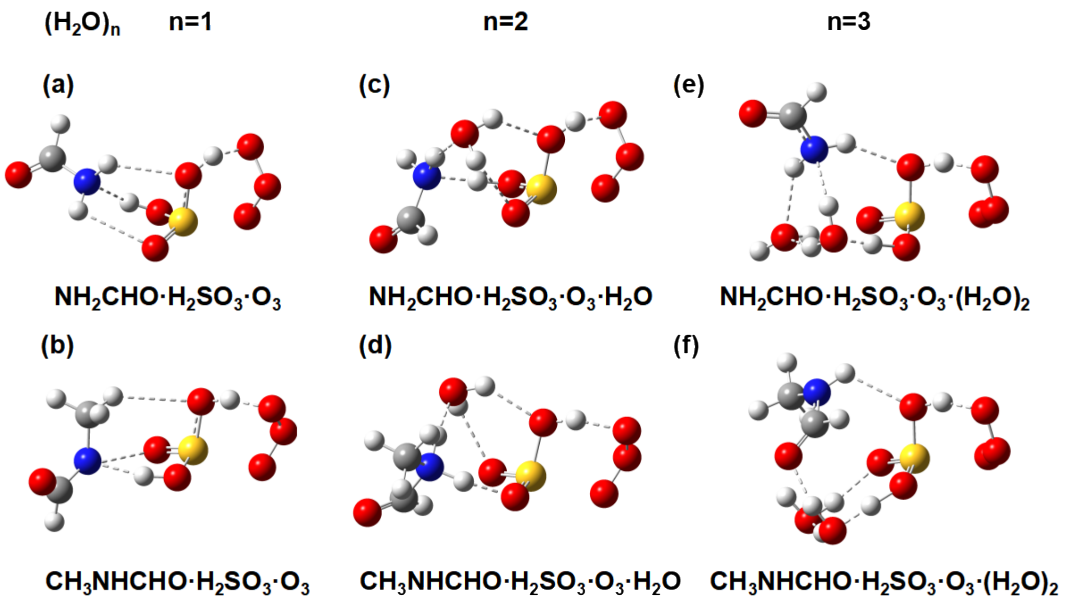

Figure S15. Structures of ozonation reaction transition state clusters (TS2) including CHO-amines.

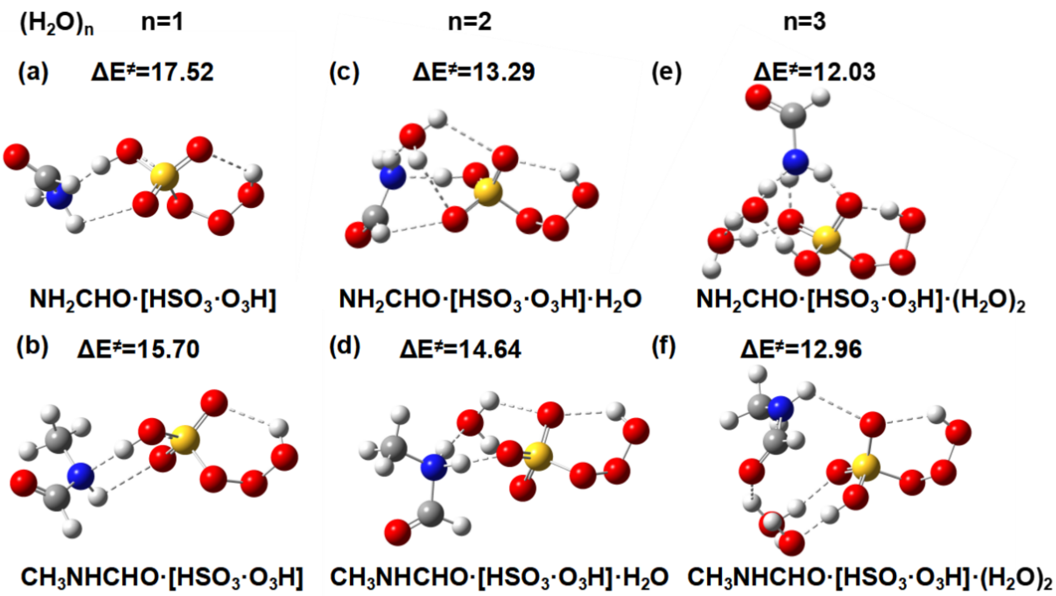

Figure S16. Structures of ozonation reaction product clusters (P3) including CHO-amines ($\Delta E^{\neq}$, in kcal/mol).

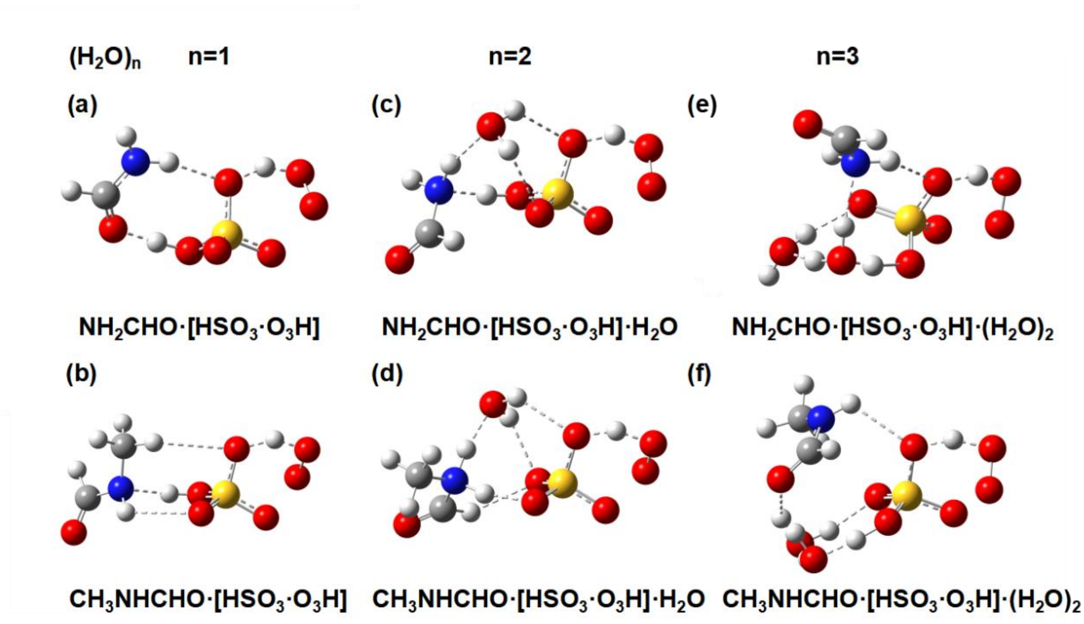

Figure S17. Structures of ozonation reaction transition state clusters (TS3) including CHO-amines.

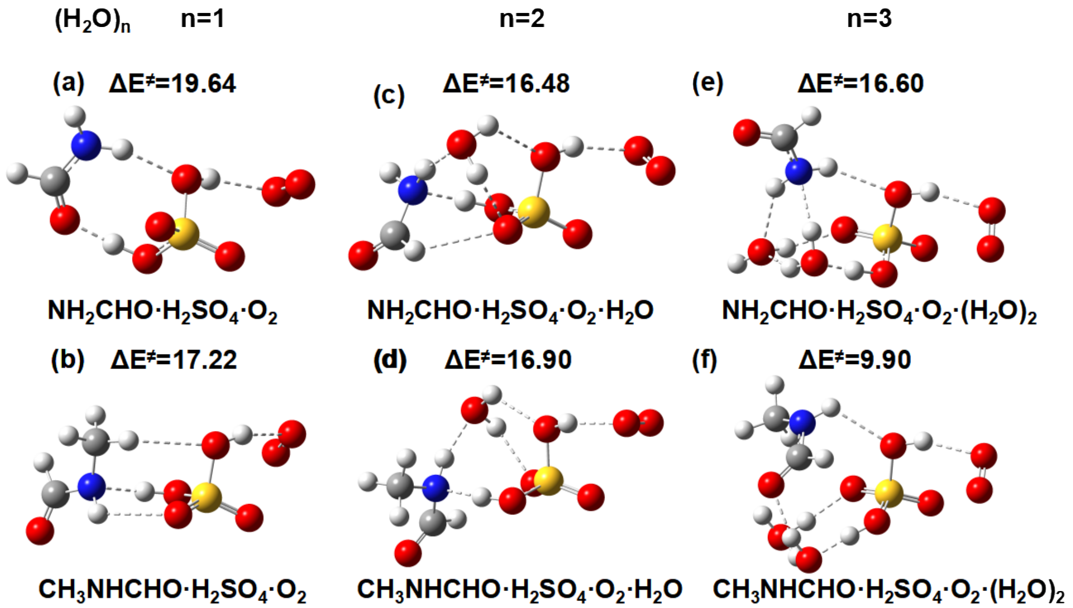

Figure S18. Structures of ozonation reaction product clusters (P4) including CHO-amines ($\Delta E^{\neq}$, in kcal/mol).

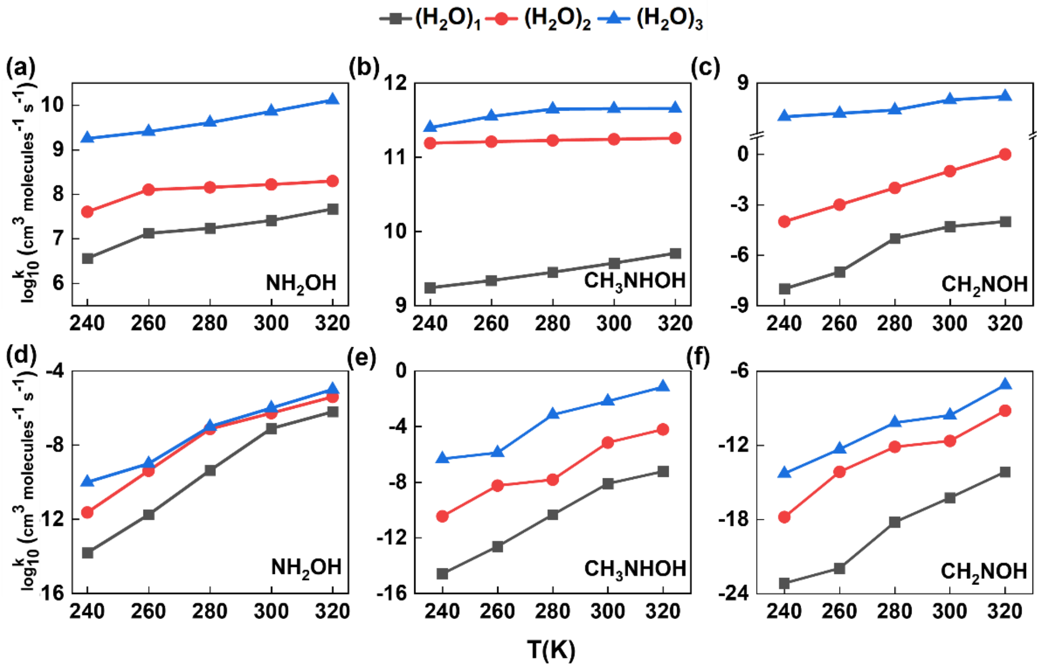

Figure S19. The influence of water content in reaction clusters and atmospheric temperature on the kinetic process of sulfate formation in the OH-amine system. (a)-(c) The changing trend of k in the SO_2 hydrolysis reaction; (d)-(f) The variation trend of k in the ozonation reaction of H_2SO_3.

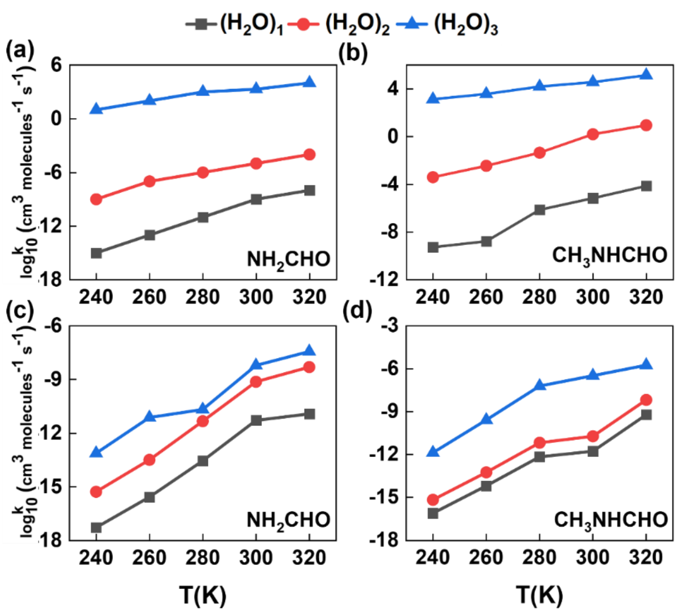

Figure S20. The influence of water content in reaction clusters and atmospheric temperature on the kinetic process of sulfate formation in the CHO--amine system. (a)-(b) The changing trend of k in the SO_2 hydrolysis reaction; (c)-(d) The variation trend of k in the ozonation reaction of H_2SO_3.

Table S1. Unimolecular rate constants (k, in cm^3 $molecules^{-1}$ s^{-1}) for the hydrolysis and ozonation reactions (n = 1) at temperatures of 240 K ~ 320 K.

	SO_2 hydrolysis	H_2SO_3 ozonation
NH_2OH	5.59×10^{6} ~ 6.68×10^{7}	8.08×10^{-13} ~ 2.06×10^{-6}
CH_3NHOH	2.41×10^{9} ~ 7.06×10^{9}	5.87×10^{-14} ~ 2.26×10^{-7}
CH_2NOH	3.10×10^{-8} ~ 7.71×10^{-4}	1.69×10^{-23} ~ 1.53×10^{-14}
NH_2CHO	9.78×10^{-15} ~ 2.27×10^{-8}	2.77×10^{-17} ~ 9.22×10^{-10}
CH_3NHCHO	2.73×10^{-9} ~ 1.39×10^{-4}	1.10×10^{-16} ~ 2.26×10^{-9}

Table S2. Unimolecular rate constants (k, in cm^3 $molecules^{-1}$ s^{-1}) for the hydrolysis and ozonation reactions (n = 2) at temperatures of 240 K ~ 320 K.

	SO_2 hydrolysis	H_2SO_3 ozonation
NH_2OH	6.05×10^{7} ~ 2.96×10^{8}	6.31×10^{-11} ~ 3.99×10^{-5}
CH_3NHOH	1.91×10^{11} ~ 2.57×10^{11}	4.52×10^{-10} ~ 2.06×10^{-4}
CH_2NOH	6.76×10^{-4} ~ 2.16×10^{0}	8.10×10^{-17} ~ 1.94×10^{-9}
NH_2CHO	9.19×10^{-9} ~ 7.18×10^{-4}	2.76×10^{-15} ~ 3.07×10^{-8}
CH_3NHCHO	4.00×10^{-3} ~ 9.57×10^{0}	1.74×10^{-15} ~ 1.86×10^{-8}

Table S3. Unimolecular rate constants (k, in cm^3 $molecules^{-1}$ s^{-1}) for the hydrolysis and ozonation reactions (n = 3) at temperatures of 240 K ~ 320 K.

	SO_2 hydrolysis	H_2SO_3 ozonation
NH_2OH	2.53×10^{9} ~ 1.16×10^{10}	1.57×10^{-10} ~ 8.64×10^{-5}
CH_3NHOH	4.23×10^{11} ~ 6.57×10^{11}	3.22×10^{-6} ~ 1.54×10^{-1}
CH_2NOH	2.29×10^{7} ~ 1.90×10^{8}	2.84×10^{-14} ~ 1.21×10^{-7}
NH_2CHO	5.87×10^{1} ~ 1.29×10^{4}	1.22×10^{-13} ~ 4.36×10^{-7}
CH_3NHCHO	1.37×10^{3} ~ 1.43×10^{5}	8.76×10^{-11} ~ 7.56×10^{-5}