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1 Supplementary information for "Kinetics of the Oxidation of Ammonia and

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Amines with Hydroxyl Radicals in the Aqueous Phase"

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8 This part includes: Kinetic data for ammonia, DMA and DEA against OH under different pH

9 (Table S1), the temperature trend over time in the photo-reactor (Figure S1), and the concentration

10 change of ammonia, dimethylamine and diethtlamine in the light control and the dark control

11 experiments (Figure S2).

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Compound	рН	k _{obs} (M ⁻¹ s ⁻¹)	
	7.0	$(3.3 \pm 0.4) \times 10^{6}$	
Ammonia	7.2ª	$(3.8 \pm 0.1) \times 10^{6}$	
	9.0	$(6.2 \pm 0.6) \times 10^7$	
	9.4	$(1.4 \pm 0.2) \times 10^{8}$	
	9.7	$(1.1 \pm 0.2) \times 10^{8}$	
	10.0	$(1.7 \pm 0.4) \times 10^{8}$	
	7.0	$(1.02 \pm 0.04) \times 10^7$	
	9.0	$(6.0 \pm 0.6) \times 10^7$	
Dimethylamine	10.2	$(7.0\pm0.1) imes10^8$	

13 Table S1. Kinetic data for ammonia, DMA and DEA against OH under different pH

	10.5	$(1.3 \pm 0.1) \times 10^9$
	10.7	$(1.8 \pm 0.5) \times 10^9$
	11.0	$(2.2 \pm 0.4) \times 10^{8}$
	7.4	$(1.7 \pm 0.1) \times 10^8$
Diethylamine	7.4 ^b	$(1.7 \pm 0.03) \times 10^8$
	10.0	$(7.0 \pm 1.0) \times 10^{8}$
	10.4	$(1.18 \pm 0.04) \times 10^9$
	10.5	$(1.5\pm0.1)\times10^8$
	10.8	$(1.9 \pm 0.2) \times 10^8$
	11.0	$(3.01 \pm 0.17) \times 10^9$

- 14 **a**Performed under a single 254nm UVB light radiation with sample solution inside a 1L Wheaton media bottle.
- 15 ^bRepetition at pH = 7.4 and was not included in linear regression analysis between the f value and k_{obs} .
- 16



- 18 Figure S1. The temperature trend in the photo-reactor over 5.3 hours. I-button was placed into the chamber 19 at 0 hour to monitor the temperature change, and was taken out of the chamber every hour.
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Figure S2. (a) Light and (b) dark control experiments of ammonia, dimethylamine and diethylamine in the presence of reference compounds. In the light control experiment, a sample solution containing ~0.2mM of each compound without the addition of H₂O₂ was placed in the photo-reactor over 5 hours; in the dark control experiments, a sample solution containing ~0.2mM of all compounds with ~100mM of H₂O₂ was placed in a dark environment over 6 days.

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The concentration of compounds of interest and reference compounds were measured by a cation 28 and an anion Dionex ICS-2000 Ion Chromatography systems (ThermoFisher Scientific, USA) 29 coupled with an AS40 auto-sampler (ThermoFisher Scientific, USA). For the measurement of 30 ammonia, the cation eluent was set as 0.6mM from 0 to 60 min. For the measurement of DMA and 31 DEA, the cation eluent gradient was set as 1 mM to 2 mM from 0 to 20 min, and kept 2mM from 32 20 to 32 min. For anion measurements, the eluent was set as 10 mM from 0 to 13 min, 10 mM to 33 45 mM from 13 to 25 min, and returned to 10 mM at 32 min. The flow rate was set as 1 mL/min 34 for all measurements. 35



Figure S3. The cation chromatogram for DEA oxidations with OH radicals at pH = 10.8 showing the decay of DEA and the formation of products.

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- 40 Table S2. Comparison of the kinetic data between compounds of interest in our study with corresponding
- 41 carboxylic acids that have the similar numbers of hydrogen atoms for abstraction

Compound	k _{BH}	k _{BH+}	k_{BH}/k_{BH^+}	References
Ammonia	1.76×10^{8}	2.31×10^{6}	76	This study
DMA	3.33×10^{9}	9.48×10^{6}	351	This study
DEA	4.95×10^{9}	1.45×10^{8}	34	This study
Compound	k _{A-}	k _A	k _A -/k _A	References
Acetic acid	8.50×10^{7}	1.60×10^{7}	5	Buxton et al. ¹
Propionic acid	8.20×10^{8}	2.90×10^{8}	3	Buxton et al. ¹
Isovaleric acid	2.40×10^{9}	1.10×10^{9}	2	Buxton et al. ¹

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43 Under three example scenarios combining gas phase, particle aqueous phase and cloud aqueous 44 phase, first order rate constant of ammonia, DMA and DEA with OH radicals and their 45 corresponding lifetimes are estimated. The parameters we used are: $[OH]_{gas} = 1 \times 10^6$ molec/cm³, 46 $[OH]_{aerosol} = 5 \times 10^{-13}$ M, $[OH]_{cloud} = 5 \times 10^{-14}$ M, $pH_{aerosol} = 3$, $pH_{cloud} = 6$, $LWC_{aerosol} = 30 \ \mu g/m^3$, 47 $LWC_{cloud} = 1 \ g/m^3,^{2-4} \ k(NH_3, OH)_{gas} = 1.6 \times 10^{-13} \ cm^3/(molec \cdot s),^5 \ k(DMA, OH)_{gas} = 6.5 \times 10^{-11}$ 48 $cm^3/(molec \cdot s),^6 \ k(DEA, OH)_{gas} = 7.4 \times 10^{-11} \ cm^3/(molec \cdot s),^7 \ k_H(NH_3) = 6.0 \ x \ 10^{-1} \ mol/(m^3 \cdot Pa),$ 49 $k_H(DMA) = 5.6 \ x \ 10^{-1} \ mol/(m^3 \cdot Pa)$ and $k_H(DEA) = 3.9 \ x \ 10^{-1} \ mol/(m^3 \cdot Pa).^{8,9}$ The estimated first

- 50 order loss rate constants are calculated using following equations:
- 51 First order rate constant in aerosol/cloud

$$52 = \frac{1}{1 + k_{Heff} \cdot LWC} \cdot k_{obs} \cdot [OH]_{aerosol or cloud}$$

53 First order rate constant in the gas phase

$$54 = \frac{k_{Heff} \cdot LWC}{1 + k_{Heff} \cdot LWC} \cdot k_{gas} \cdot [OH]_{gas}$$

55 Where k_{Heff} = The effective Henry's law constant = $k_H(1 + \frac{[H^+]}{k_a})$, LWC is the liquid water 56 content, k_{obs} is the observed rate constant of ammonia/amines at a specific pH, which calculation 57 is shown in the main text, k_{gas} is the literature value for the gas phase rate constant.

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