Supporting Information

T- and pH-dependent OH radical reaction kinetics with glycine, alanine, serine, and threonine in aqueous phase

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Contents

Calculation of the statistical error

The errors of rate constants are calculated as the Eq. (S1):

$$\Delta k = \frac{\sqrt{\sum((\frac{A[(SCN)_2\cdot^-]_o}{A[(SCN)_2\cdot^-]_x}-1-\frac{k_{RH}[RH]}{k_{ref}[SCN^-]})/(\frac{\Delta A[(SCN)_2\cdot^-]_o}{A[(SCN)_2\cdot^-]_o}+\frac{\Delta A[(SCN)_2\cdot^-]_x}{A[(SCN)_2\cdot^-]_x}))^2}}{2\times\sqrt{\sum(\frac{[RH]}{[SCN^-]})^2/(\frac{\Delta A[(SCN)_2\cdot^-]_o}{A[(SCN)_2\cdot^-]_o}+\frac{\Delta A[(SCN)_2\cdot^-]_x}{A[(SCN)_2\cdot^-]_x})^2}} \quad \text{(S1)}$$

$$\Delta A[(SCN)_2\cdot^-] = A \times S/\sqrt{n} \quad \text{(S2)}$$

$A[(SCN)_2\cdot^-]$ represents the maximum absorbance during measurement. The [RH] and [SCN^-] are the concentrations of amino acids and SCN^-, respectively. The k_{RH} and k_{ref} represent the rate constants of the amino acids and SCN^- ion, respectively, in the reactions with the OH radicals. Besides, considering a confidence interval of 95% in the two-sided Student's *t*-test, the standard error of $\Delta A[(SCN)_2\cdot^-]$ can be calculated as in Eq. (S2). The standard deviation and the number of samples are expressed by *S* and *n*, respectively. The parameter *A* is 2.365 according to the sample number of 8 in the Student's *t*-distribution.

Molar absorption coefficient

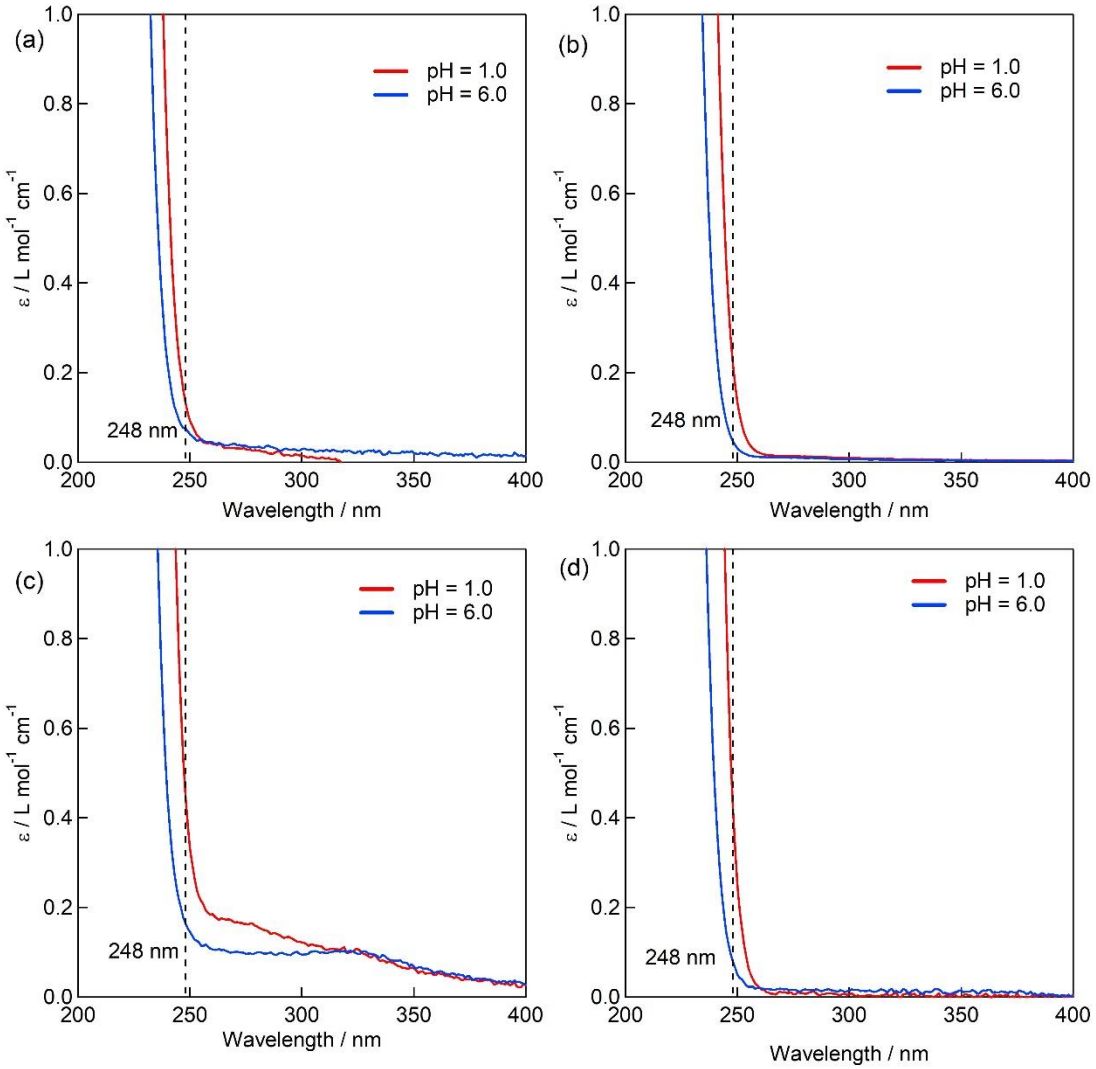


Fig. S1. Molar absorption coefficients (ε) of (a) glycine, (b) alanine, (c) serine, and (d) threonine in a wavelength range of 200 – 400 nm at the pH values of 1.0 and 6.0. The ε values were measured at the concentration of 0.1 mol L^{-1} for Gly and Ala, as well as at the concentration of 0.01 mol L^{-1} for Ser and Thr.

pH-dependent ionization

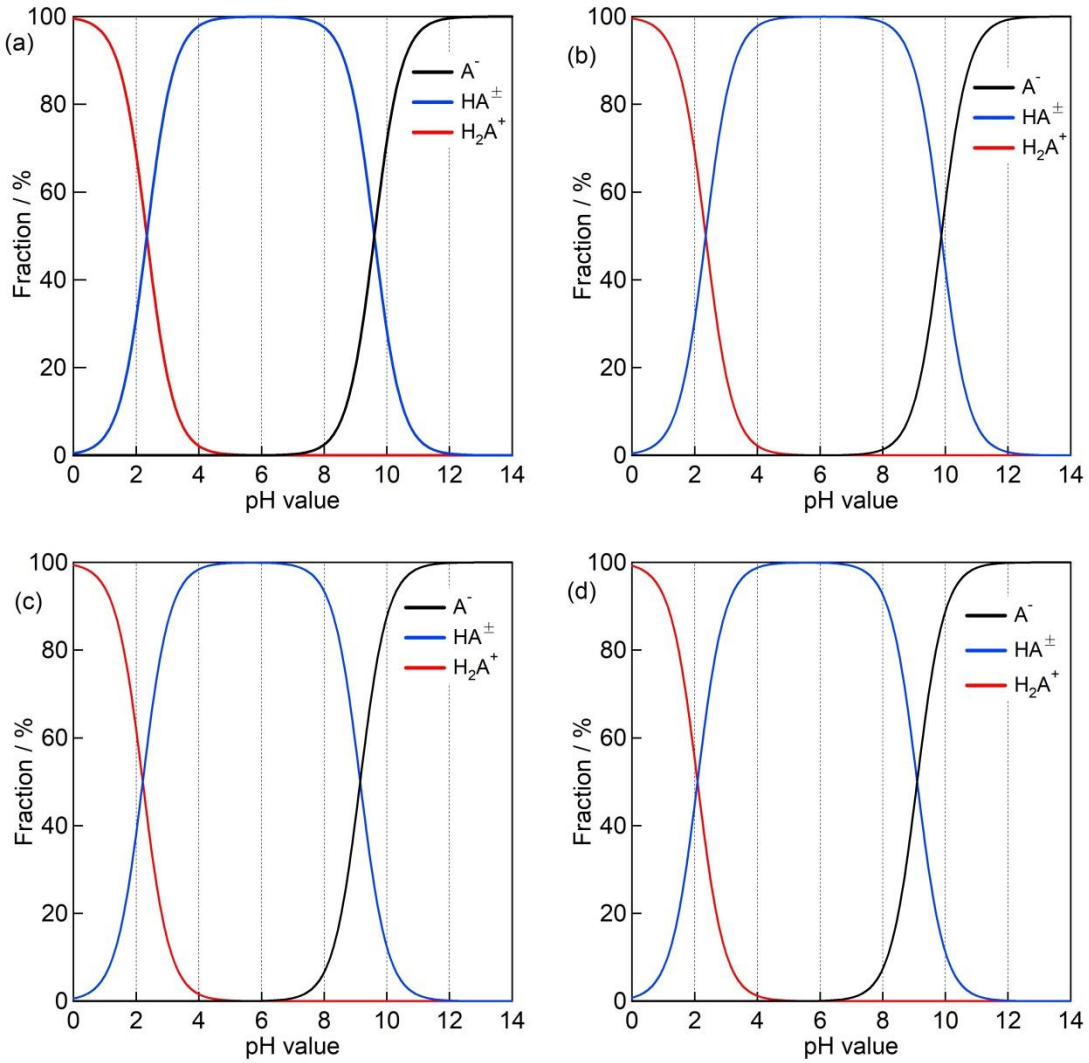


Fig. S2. Fractions of H_2A^+, $HA^{\pm}$ and A^- in (a) glycine, (b) alanine, (c) serine, and (d) threonine as a function of pH values of the solutions.

Diffusion rate constant calculation

The Smoluchowski equation (Eq. (S3)) is used to calculate the diffusion rate constant (k_D) at the pH value 6.0 (see Table S1).[1, 2] The N_A represents the Avogadro constant, and the r_{OH} and $r_{Reac.}$ express the radii of the OH radical and the amino acid. The diffusion coefficients of the OH radical and the reactants (D_{OH} and D_{Reac}) are calculated by the Eq. (S4), where X, M, T, η and V_m represent the association parameter of water (2.26), the molar mass of water, the temperature, the viscosity of water and the molar hard-core volume, respectively. According to the method and the related parameters in previous studies,[3, 4] the V_m of the OH radical, glycine, alanine, serine and threonine are calculated as 26.9, 71.0, 90.3, 97.7 and 117.3 cm^3 mol^{-1}, and the r_{Reac} are 0.22, 0.30, 0.33, 0.34 and 0.36 nm, respectively.

$$k_D = \frac{4\times\pi\times N_A\times(r_{OH}+r_{Reac.})\times(D_{OH}+D_{Reac.})}{1000} / \, L\, mol^{-1}s^{-1} \qquad \text{(S3)}$$

$$D = 7.4\times10^{-8}\times\frac{\sqrt{(X\times M)}\times T}{V_m^{0.6}\times\eta} / \, cm^2 s^{-1} \qquad \text{(S4)}$$

Table S1. Diffusion coefficients D and diffusion rate constant k_D of the OH radical reactions with glycine, alanine, serine, and threonine.

T / K	D ×10^{-6} cm^2 s^{-1}				k_D ×10^{10} L mol^{-1} s^{-1}			
	Gly	Ala	Ser	Thr	Gly	Ala	Ser	Thr
278	12.0	12.0	12.0	12.0	0.9	0.9	0.9	0.9
288	16.6	16.6	16.6	16.6	1.1	1.1	1.1	1.1
298	21.9	21.9	21.9	21.9	1.4	1.4	1.4	1.4
308	28.1	28.1	28.1	28.1	1.6	1.6	1.6	1.6
318	35.1	35.1	35.1	35.1	1.9	1.9	1.9	1.9

Comparison of rate constant and energy barrier

$$Z = \sum \frac{n_H}{\Delta G_b} \qquad \text{(S5)}$$

Table S2. Reaction rate constants and Z values of protonated glycine, acetic acid, methylamine, alanine, propionic acid, ethylamine, serine, threonine, glutaric acid and adipic acid with the OH radicals. The value of Z is calculated as Eq. (S5). [5-9]

	k_{2nd} / L mol^{-1} s^{-1}	log k_{2nd} / L mol^{-1} s^{-1}	Z / mol kJ^{-1}
Glycine	3.3×10^6	6.52	0.09
Acetic acid	1.4×10^7	7.15	0.07
Methylamine	1.9×10^7	7.28	0.10
Alanine	3.6×10^7	7.56	0.13
Propionic acid	3.8×10^8	8.58	0.13
Ethylamine	1.2×10^8	8.08	0.15
Serine	3.3×10^8	8.52	0.15
Threonine	4.3×10^8	8.62	0.19
Glutaric acid	5.5×10^8	8.74	0.16
Adipic acid	1.4×10^9	9.15	0.20

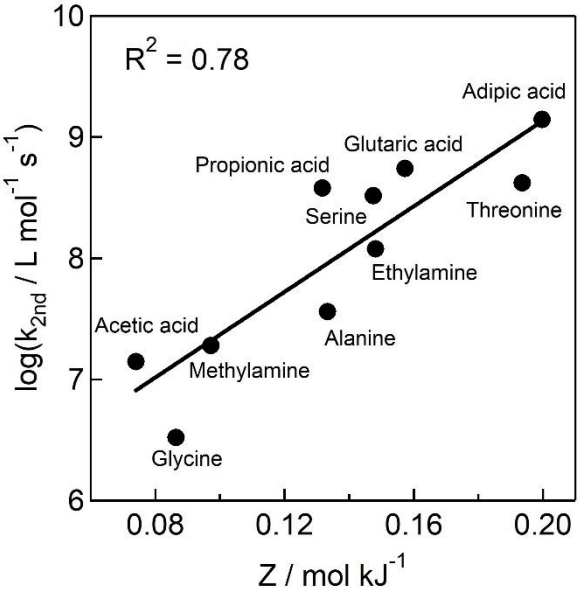


Fig. S3. Correlation between log(k_{2nd}) and Z for glycine, acetic acid, methylamine, alanine, propionic acid, ethylamine, serine, threonine, glutaric acid and adipic acid.[5-9]

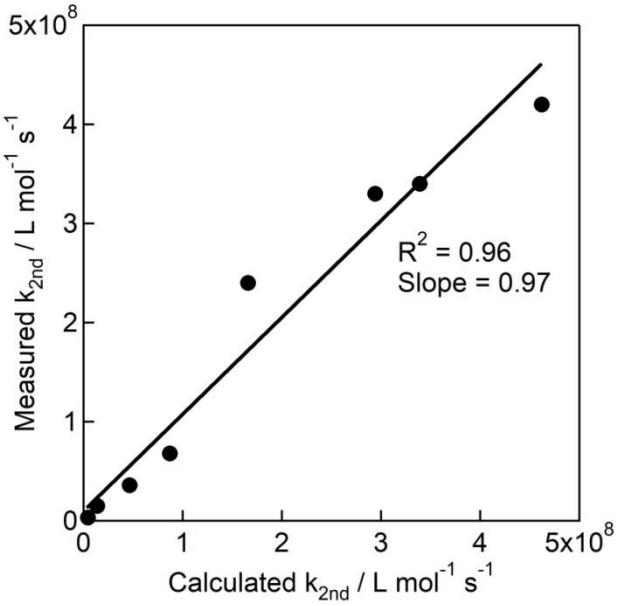
Structure-activity relationships calculation

Table S3. Group rate constants and contribution factors in the SAR calculation developed by Monod and Doussin[10].

	Group rate constant	Contribution factor	
	/ L mol^{-1} s^{-1}	Next 1	Next 2
–COOH	——	0.07	0.70
$–COO^-$	——	0.24	1.23
–OH	6.9×10^7	2.10	0.44
$–CH_3$	3.5×10^8	1.33	1.17
$–CH_2–$	6.5×10^8	1.21	1.10
–CH<	4.7×10^8	1.11	1.05

Table S4. Group rate constants and contribution factors in the SAR calculation developed by Minakata et al[11].

	Group rate constant	Contribution factor
	/ L mol^{-1} s^{-1}	Next 1
–COOH	7.0×10^5	0.04
–OH	1.0×10^8	0.58
$–CH_3$	1.2×10^8	1.12
$–CH_2–$	5.1×10^8	1.17
–CH<	2.0×10^9	1.17
$–NH_2$	4.0×10^9	1.63



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101 **Fig. S4.** Measured ·OH rate constants of protonated and zwitterionic Gly, Ala, Ser, and Thr against

102 the estimated rate constants by the improved SAR calculation developed by Monod and Doussin[10].

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