Carbon-Centered Radicals Add Reversibly to Histidine – Implications

Supplementary Information

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Fig. S1: Absorption at 360 nm, 5 µs after irradiation (50 Gy) of N₂O saturated aqueous solutions of 1 M t-BuOH containing variable amounts of HisNH₂. The optical pathlength is 6 cm. The curve represents a fit for $K = 3 \times 10^3$ M⁻¹ and $\varepsilon_{360nm}([\text{HisNH}_2^-\cdot\text{t-BuOH}]) = 4 \times 10^5$ M⁻¹cm⁻¹. At [HisNH₂] > 3 mM the absorption increases unexpectedly.
**Fig. S2:** Plot of $1/k_{\text{obs}}$ vs. [HisNH$_2$] for the decay of absorption after irradiation (50 Gy) of N$_2$O saturated aqueous solutions of 1 M t-BuOH containing variable amounts of HisNH$_2$. Because we are using absorption data and not concentration data, the observed rate constant ($k_{\text{obs}}$) is dependent both on the difference in molar absorptivity between products and reactants ($\Delta \varepsilon$) and the optical pathlength ($l$), $k_{\text{obs}} = 2k_{2.0}/(\Delta \varepsilon \times l)$. Due to equilibrium 5, the second order rate constant $k_{2.0}$ is dependent on the availability of free t-*BuOH: $k_{2.0} = k_6/(1+K_5[\text{HisNH}_2])$. With $k_{\text{obs}} \times \Delta \varepsilon \times l = 2k_6/(1+K_5[\text{HisNH}_2])$, a plot $1/k_{\text{obs}}$ vs. [HisNH$_2$] follows the equation $y = ((1+K_5[\text{HisNH}_2]) \times \Delta \varepsilon \times l) / 2k_6$. So, slope $= K_5 \times \Delta \varepsilon \times l / 2k_6$, offset $= \Delta \varepsilon \times l / 2k_6$ and $K_5 = \text{slope}/\text{offset}$. We find $K_5 \approx 4 \times 10^3$ M$^{-1}$ at low concentrations. At [HisNH$_2$] $\approx$ 3 mM, the slope changes distinctly and the chemical reactions responsible for the absorbance decay must change, too.
**Fig. S3**: Spectrum of N₂O saturated aqueous solutions containing 4.1 mM HisNH₂ and 10 % MeOH (v/v), 2 µs after irradiation (50 Gy, optical pathlength 6 cm). Under these conditions, H-atoms are scavenged quantitatively and the curve is dominated by the adduct of the hydroxymethyl radical to HisNH₂. Two maxima at around 300 nm and 360 nm are visible. Hydroxymethyl radicals contribute to the observed absorption at $\lambda < 320$ nm.