Electronic Supplementary Material (ESI) for Chemical Communications.

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 N_2O saturated aqueous solutions of 1 M *t*-BuOH containing variable amounts of $HisNH_2$. The optical pathlength is 6 cm. The curve represents a fit for $K_5 = 3\times10^3$ M^{-1} and $\varepsilon_{360nm}([HisNH_2^{\cdot\cdot}t\text{-BuOH}]^{\bullet}) = 4 \times 10^2$ $M^{-1}cm^{-1}$. At $[HisNH_2] > 3$ mM the absorption increases unexpectedly.

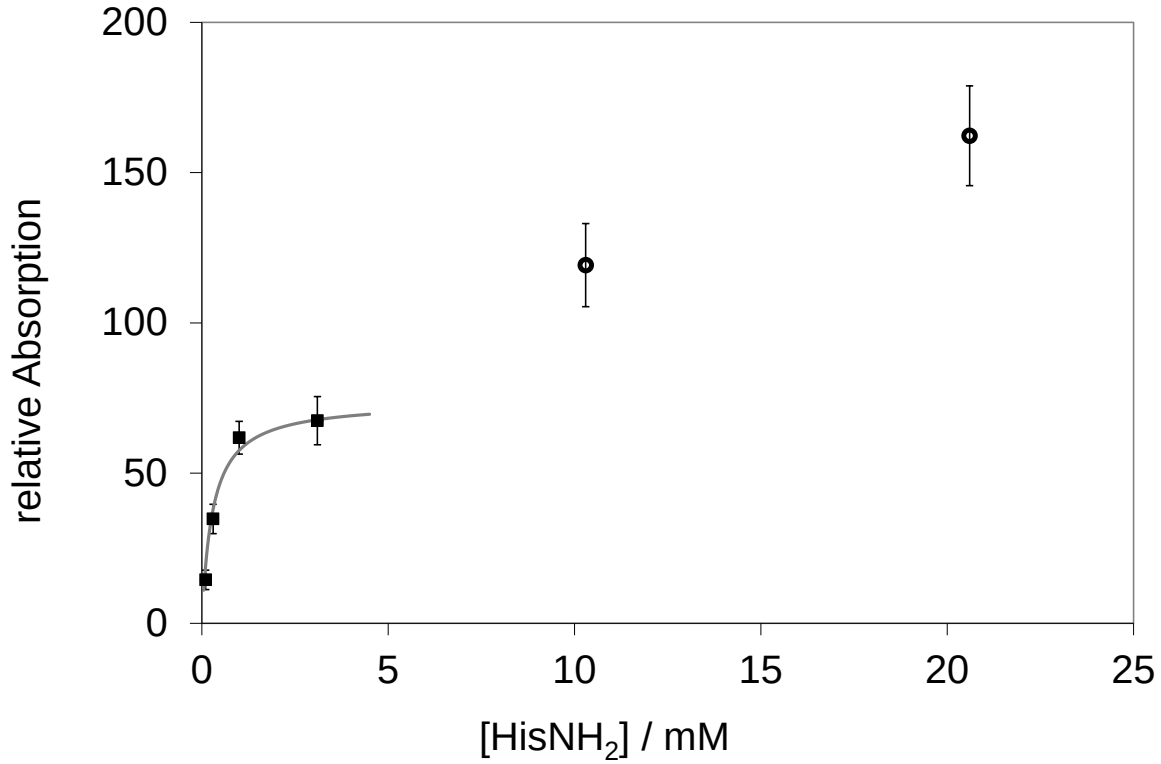

Fig. S2: Plot of $1/k_{obs}$ *vs.* $[HisNH_2]$ for the decay of absorption after irradiation (50 Gy) of N_2O saturated aqueous solutions of 1 M *t*-BuOH containing variable amounts of $HisNH_2$. Because we are using absorption data and not concentration data, the observed rate constant (k_{obs}) is dependent both on the difference in molar absorptivity between products and reactants ($\Delta\varepsilon$) and the optical pathlength (l), $k_{obs} = 2k_{2.O}/(\Delta\varepsilon \times l)$. Due to equilibrium 5, the second order rate constant $k_{2.O}$ is dependent on the availability of free *t*-$^{\bullet}$BuOH: $k_{2.O} = k_6/(1+K_5[HisNH_2])$. With $k_{obs} \times \Delta\varepsilon \times l = 2k_6/(1+K_5[HisNH_2])$, a plot $1/k_{obs}$ *vs.* $[HisNH_2]$ follows the equation $y = ((1+K_5[HisNH_2]) \times \Delta\varepsilon \times l) / 2k_6$. So, slope = $K_5 \times \Delta\varepsilon \times l / 2k_6$, offset = $\Delta\varepsilon \times l / 2k_6$ and K_5 = slope/offset. We find $K_5 \approx 4\times10^3$ 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.

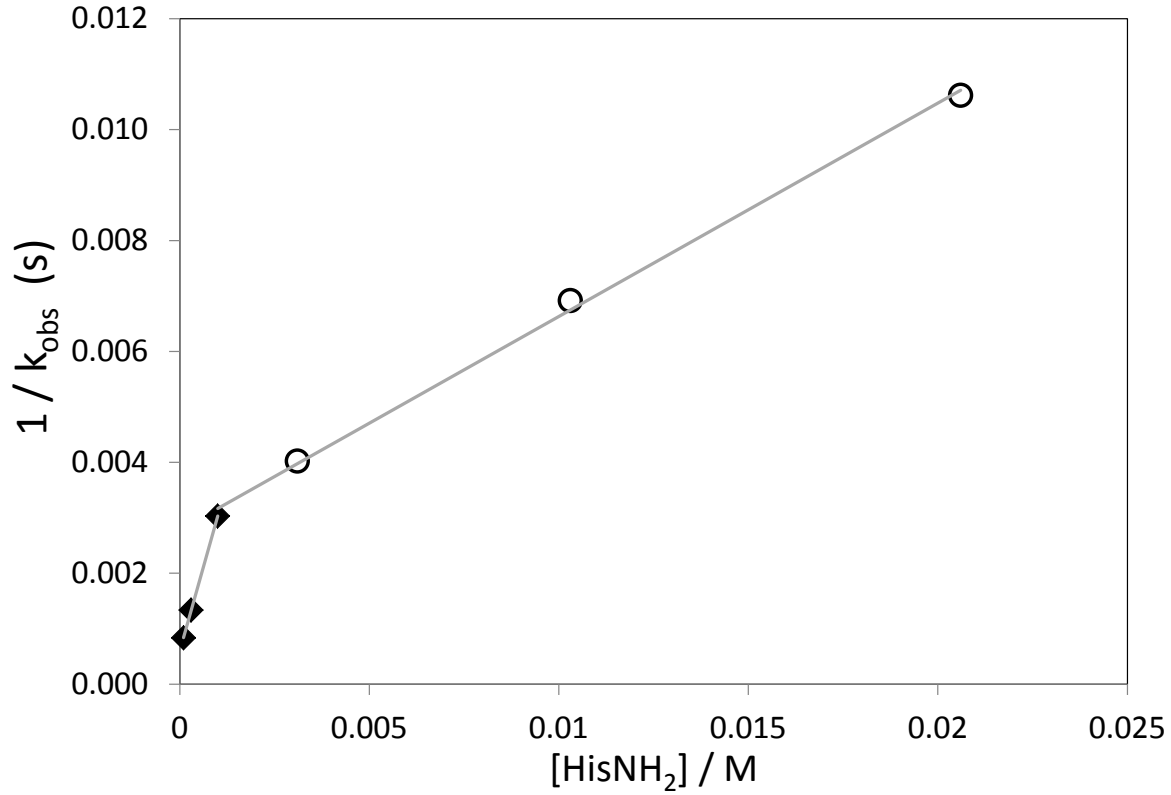

Fig. S3: Spectrum of N_2O saturated aqueous solutions containing 4.1 mM $HisNH_2$ and 10 % MeOH (v/v) , 2 µs after irradiation (50 Gy, optical pathlength 6 cm). Under these conditions, H-atoms are scavenged quantitatively and the curve is dominated by the adduct of the hydroxymethyl radical to $HisNH_2$. Two maxima at around 300 nm and 360 nm are visible. Hydroxymethyl radicals contribute to the observed absorption at $\lambda < 320$ nm.