

Supporting Information to:

Changing the Direction of Intramolecular Electron Transfer in Oxidized Dipeptides Containing Tryptophan and Tyrosine

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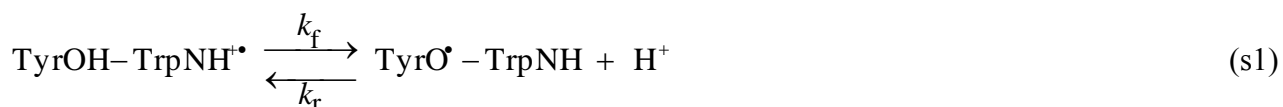
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Modeling of CIDNP kinetics in photoreaction of 2,2'-dipyridyl with tyrosine-tryptophan

To simulate CIDNP kinetics obtained during photoreaction of 2,2'-dipyridyl with Tyr-Trp we applied an approach suggested by Fischer and co-authors¹ and modified it to take into account intramolecular electron transfer (IET) from tyrosine residue to tryptophanyl radical with the rate constant k_f and from tryptophan residue to tyrosyl radical with the rate constant k_r ($K=k_f/k_r$):



The time dependence of the concentrations of radicals derived from dipyrityl R_D , tryptophan R_{Trp} , and tyrosine R_{Tyr} is described by equations s2-s4:

$$R_D(t) = \frac{R_0}{1 + k_t R_0 t} \quad (\text{s2})$$

$$R_{\text{Trp}}(t) = \frac{\frac{R_0}{1+K} + \frac{\chi K R_0 - (1-\chi)R_0}{1+K} e^{-(k_t+k_r)t}}{1+k_t R_0 t} \quad (\text{s3})$$

$$R_{\text{Tyr}}(t) = \frac{\frac{K R_0}{1+K} - \frac{\chi K R_0 - (1-\chi)R_0}{1+K} e^{-(k_t+k_r)t}}{1+k_t R_0 t} \quad (\text{s4})$$

Here k_t is the second-order radical termination rate constant. We neglect the fraction of geminate recombination and consider the formation of radical pairs as instantaneous; thus, R_0 is the initial concentration of radical pairs. The initial concentration of radicals is: R_0 for $\text{DPH}_2^{+\bullet}$, χR_0 for $\text{TyrOH-TrpNH}^{+\bullet}$, $(1-\chi)R_0$ for $\text{TyrO}^\bullet\text{-TrpNH}$.

Polarization in the dipyridyl radical (P_D^R) and the ground state dipyridyl (P_D) is written as follows:

$$\frac{dP_D^R}{dt} = -k_t P_D^R (R_{\text{Trp}} + R_{\text{Tyr}}) - k_t \beta_1 R_D R_{\text{Trp}} - k_t \beta_2 R_D R_{\text{Tyr}} - \frac{P_D^R}{T_{1(D)}} \quad (\text{s5})$$

$$\frac{dP_D}{dt} = k_t P_D^R (R_{\text{Trp}} + R_{\text{Tyr}}) + k_t \beta_1 R_D R_{\text{Trp}} + k_t \beta_2 R_D R_{\text{Tyr}} \quad (\text{s6})$$

In equations s5 and s6, two types of radical pairs are considered. The first and second terms describe polarization transfer from the radical to the ground state molecule in the termination with the radicals $\text{TyrOH-TrpNH}^{+\bullet}$ and $\text{TyrO}^\bullet\text{-TrpNH}$, respectively. The third and forth terms refer to polarization formation in radical pairs in the bulk, i. e. the so-called F-pairs. The last term in equation s5 describes nuclear paramagnetic relaxation with the time $T_{1(D)}$. The polarization, created in F-pairs is related to the parameter β proportional to the value of geminate polarization P^G : $\beta = \gamma P^G / R_0$. The quantity γ is the ratio of CIDNP created in geminate and in F-pairs, and is believed to be equal to 3 in the case of a triplet precursor.¹ In accordance with the literature $\beta = 2.8 P^G / R_0$ was used.¹ For modeling the formation of CIDNP for dipyridyl in the two types of radical pairs we introduced the values β_1 and β_2 in equations s5 and s6: $\beta_1 = \gamma P^{G1} / (\chi R_0)$, $\beta_2 = \gamma P^{G2} / ((1-\chi)R_0)$. According to the spin-sorting nature of the mechanism of CIDNP formation at high magnetic field, the initial conditions are: $P_D(0) = -P_D^R(0) = P^{G1} + P^{G2}$. Since

CIDNP is measured in arbitrary units, in our simulations $P_D(0)$ appears as scaling factor. From the comparison of signal intensities in geminate CIDNP spectra of Trp-Tyr (for which $\chi=0.6$)⁸ with that of Tyr-Trp, it was found that for Tyr-Trp $\chi=0.7$ and that CIDNP formed for DP in the radical pair with tryptophanyl radical is 1.5 times higher in amplitude than CIDNP formed for DP in the radical pair with tyrosyl radical.

The rate constants k_f and k_r do not explicitly show up in equations s5 and s6, however, the reactions of IET have influence on the CIDNP kinetics of dipyrityl via the radical concentrations R_{Trp} and R_{Tyr} .

The reversibility of electron transfer together with the presence of degenerate electron exchange requires that polarization of tryptophan protons be considered in three types of particles: with the radical center at the tryptophan moiety (P_{Trp}^R), with the radical center at the tyrosine moiety (P_{Trp}^r), and in the ground state peptide (P_{Trp}):

$$\frac{dP_{\text{Trp}}^R}{dt} = -k_t P_{\text{Trp}}^R R_D - k_t \beta R_D R_{\text{Tyr}} - k_{\text{ex}} C P_{\text{Trp}}^R - k_f P_{\text{Trp}}^R + k_r P_{\text{Trp}}^r - \frac{P_{\text{Trp}}^R}{T_{1(\text{Trp})}} \quad (\text{s7})$$

$$\frac{dP_{\text{Trp}}^r}{dt} = -k_t P_{\text{Trp}}^r R_D + k_f P_{\text{Trp}}^R - k_r P_{\text{Trp}}^r \quad (\text{s8})$$

$$\frac{dP_{\text{Trp}}}{dt} = k_t P_{\text{Trp}}^R R_D + k_t \beta R_D R_{\text{Tyr}} + k_t P_{\text{Trp}}^r R_D + k_{\text{ex}} C P_{\text{Trp}}^R \quad (\text{s9})$$

Equations s7-s9 do not only contain the terms of second-order radical termination and paramagnetic relaxation, but also the terms relating to the polarization transfer in the reactions of IET and degenerate electron exchange. The chemical shift of tryptophan protons in the peptide with electron deficient tyrosine can differ from that in the diamagnetic peptide due to a small Knight shift. However, the FT-NMR signal acquisition starts 500 μs after the excitation pulse, when all radicals have decayed, hence the polarizations P_{Trp}^r and P_{Trp} are detected together. Thus, the experimental points in Figure 3 of the manuscript correspond to $P_{\text{Trp}}^r + P_{\text{Trp}}$.

Similarly, equations s10-s12 describe the polarization of tyrosine protons in the tyrosine-centered radical TyrO[•]-TrpNH ($P_{\text{Tyr}}^{\text{R}}$), the tryptophan-centered radical TyrOH-TrpNH^{•+} ($P_{\text{Tyr}}^{\text{r}}$), and the ground state peptide TyrOH-TrpNH (P_{Tyr}):

$$\frac{dP_{\text{Tyr}}^{\text{R}}}{dt} = -k_t P_{\text{Tyr}}^{\text{R}} R_{\text{D}} - k_t \beta R_{\text{D}} R_{\text{Tyr}} + k_f P_{\text{Tyr}}^{\text{r}} - k_r P_{\text{Tyr}}^{\text{R}} - \frac{P_{\text{Tyr}}^{\text{R}}}{T_{1(\text{Tyr})}} \quad (\text{s10})$$

$$\frac{dP_{\text{Tyr}}^{\text{r}}}{dt} = -k_t P_{\text{Tyr}}^{\text{r}} R_{\text{D}} - k_{\text{ex}} C P_{\text{Tyr}}^{\text{r}} - k_f P_{\text{Tyr}}^{\text{r}} + k_r P_{\text{Tyr}}^{\text{R}} \quad (\text{s11})$$

$$\frac{dP_{\text{Tyr}}}{dt} = k_t P_{\text{Tyr}}^{\text{R}} R_{\text{D}} + k_t \beta R_{\text{D}} R_{\text{Tyr}} + k_t P_{\text{Tyr}}^{\text{r}} R_{\text{D}} + k_{\text{ex}} C P_{\text{Tyr}}^{\text{r}} \quad (\text{s12})$$

For tyrosine, the earlier found² $\beta=1.4P^{\text{G}}/R_0$ was used. The initial conditions are: $P_{\text{Tyr}}(0)=P_{\text{Tyr}}^{\text{R}}(0)=P^{\text{G}}$,

$P_{\text{Tyr}}^{\text{r}}(0)=0$. The experimental points in Figure 2 of the manuscript correspond to $P_{\text{Tyr}}^{\text{r}} + P_{\text{Tyr}}$.

Nuclear paramagnetic relaxation times of corresponding protons are: 44 μs for H3,4 DP,³ 50 μs for β protons of Trp,⁴ 33 μs for H3,5 of Tyr³.

Finally, fitting parameters were k_r and $k_t R_0$ at each pH, k_f and k_{ex} for all pH values. The results of the best-fit simulations are shown in Figures 2-4 of the manuscript by solid lines. The parameter values are given in the text of the manuscript and in the Table 1.

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