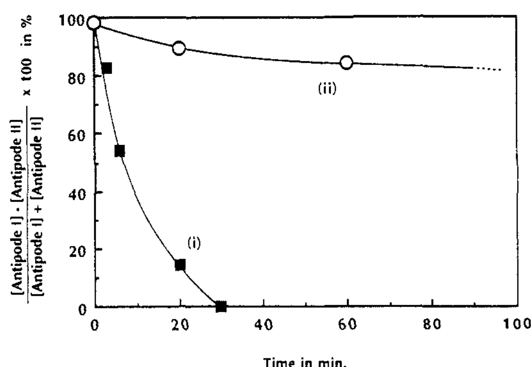

Figure 2. Racemizations of antipode I of (α-PivNHEtioP)Zn (**1b**) in hexane/EtOH/$CHCl_3$ (70/20/10 v/v, 7.1×10^{-5} M) at 28.5 °C under irradiation at 410 nm (i) and in the dark (ii). [Antipode I] and [antipode II], as determined by HPLC.

16.9 min) with significant tailing and leading in between, indicating the possibility of concomitant racemization during the HPLC separation.

The antipodes of the metal complexes **1b** and **1c** gradually racemized when stored in hexane/EtOH/$CHCl_3$ (70/20/10 v/v) at a temperature higher than 20 °C, but no racemization was observed below 0 °C.[5] In contrast, the antipodes of the free-base porphyrin (**1a**) are much easier to racemize, since antipode I with 60% enantiomeric purity, even when stored at 0 °C, gave in only 1 h an almost identical HPLC pattern as observed for racemic **1a**. The rate constants for racemization in hexane/EtOH/$CHCl_3$ (70/20/10 v/v) were measured as a function of temperature in the range 0–40 °C, which gave activation free energies (ΔG^*) of 24.2 and 21.7 kcal mol^{-1} for the thermal racemization of **1b** and **1c** at 28.5 °C. The racemization takes place via the flipping of the "amide arm" from one side of the porphyrin plane to the other through a coplanar transition state possibly as a consequence of a thermally induced conformational ruffling of the porphyrin skeleton. Thus, the above results imply that the insertion of a metal atom into the porphyrin core provides the porphyrin skeleton with enhanced ridigity, so that the thermally induced ruffling may be much restrained compared with the free-base form. Zinc porphyrins are considered to be conformationally more rigid than copper porphyrins, taking account of the higher ΔG^* value observed for **1b** than **1c**.

Of greater interest is the photoinduced racemization phenomenon observed for the antipodes of (α-PivNHEtioP)Zn (**1b**). As exemplified in Figure 2, the enantiomeric purity (enantiomeric excess, ee) of the antipode (fraction I) of **1b** decreased rapidly with time when degassed solution of the antipode (solvent: hexane/EtOH/$CHCl_3$ (70/20/10 v/v), 7.1×10^{-5} M) at 28.5 °C was exposed to monochromatized light with a wavelength of 410 nm corresponding to the Soret band,[6] and complete racemization was attained in only 30 min. In contrast, it took more than 2 days in the dark to achieve complete racemization under the same conditions. A quite similar photoinduced racemization was also observed when the antipode of **1b** was irradiated at the Q band (580 nm).[6] The quantum yields (Φ) at the initial stage upon irradiation at Soret and Q bands were 3.3×10^{-3} and 2.5×10^{-3}, respectively, during the initial 3 min at 28.5 °C.[7] Taking into account the fact that the photoinduced racemization was not quenched at all by admission of oxygen, the almost comparable quantum yields for the Soret band and Q-band excitations indicate that the photoinduced racemization originates from the singlet excited state. This is in sharp contrast with the photoinduced atropisomerization of a zinc picket-fence porphyrin, for which the triplet excited state has been implicated.[1]

Racemization of the antipodes of the copper porphyrin (**1c**) upon irradiation was also examined under similar conditions, in which however no photoacceleration effect was observed. This difference is possibly due to the short lifetimes of the photoexcited states of copper porphyrins compared with those of zinc porphyrins.[8]

In the present communication, the thermal and photoinduced conformational ruffling of distorted porphyrin skeletons is claimed, taking advantage of the successful resolution of the optical antipodes of chiral "single-armed" porphyrin complexes. Mechanistic studies on the photoinduced racemization process are in progress using other "single-armed" porphyrins with a variety of central metals.

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Supplementary Material Available: Experimental details and spectral data for compounds **1a–c** (1 page). Ordering information is given on any current masthead page.

(5) The antipodes of the homologue of **1b** with a smaller amide groups such as zinc α-(acetylamino)etioporphyrin I were also resolved, whose racemization profiles were similar to those for **1b**.

(6) A quartz cell containing **1b** or **1c** in hexane/EtOH/$CHCl_3$ (70/20/10 v/v), thermostated at 28.5 °C, was illuminated by a 300-W xenon arc lamp from a distance of 4.3 cm through a band-path filter (bandwidth 10 nm) and another filter to cut heat.

(7) Quantum yields were obtained from the change in the enantiomeric purity of **1b** during the initial 3 min, at which the contribution of the thermal racemization was negligibly small (see ii in Figure 2).

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Evidence for Through-Bond Long-Range Electron Transfer in Peptides[†]

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There are many reports of intramolecular long-range electron transfer (LRET)[1] in proteins and peptides.[2] Efficient transfer between distant donors and acceptors (i) has biological significance in photosynthesis, respiration, and enzyme-catalyzed redox reactions; (ii) may be important in mediating free-radical damage initiated by ionizing radiation and oxygen assault; and (iii) may occur in the radical processes associated with chemical carcinogenesis and cellular aging. We have, therefore, undertaken a systematic study of LRET in proteins and peptides. As part of this program we are studying the intramolecular one-electron oxidation of tyrosine (TyrOH) by the tryptophan radical (Trp•). This reaction, first elaborated by Prütz et al.,[3] is initiated with

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(1) Abbreviations: LRET, long-range electron transfer; Lys, lysine; Pro, proline; TrpH, tryptophan; TyrOH, tyrosine; Trp• and TyrO•, neutral indolyl TrpH and phenoxy TyrOH radicals; $TrpH^{\bullet+}$ and $TyrOH^{\bullet+}$, cationic TrpH and TyrOH radicals.

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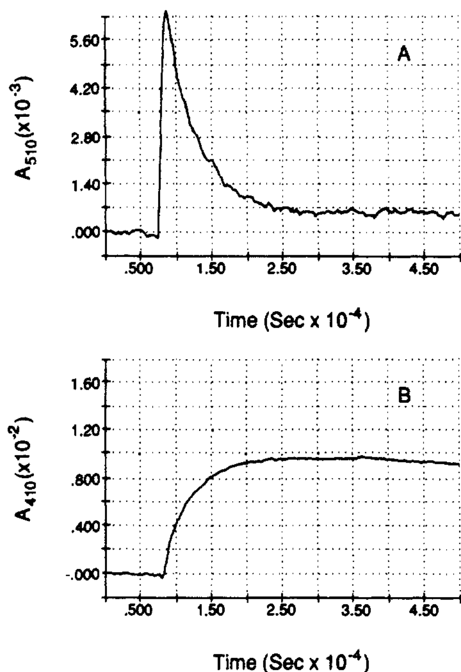
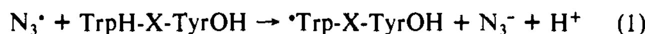


Figure 1. One-electron transfer between tyrosine and tryptophan in the peptide Lys-TrpH-Pro-TyrOH-Lys. (A) Trp$^{\bullet}$: absorbance changes at 510 nm. There are two reaction phases: an initial increase due to preferential $N_3^{\bullet}$ oxidation of TrpH to Trp$^{\bullet}$ and a slower decay due to one-electron reduction of Trp$^{\bullet}$ to TrpH. (B) TyrO$^{\bullet}$: absorbance changes at 410 nm. After an initial small increase due to the less favored $N_3^{\bullet}$ oxidation of TyrOH to TyrO$^{\bullet}$, there is a subsequent first-order intramolecular oxidation of TyrOH to TyrO$^{\bullet}$ that is simultaneous with the Trp$^{\bullet}$ reduction shown in panel A. The concentration of peptide was 0.2 mM, with N_3^- and $N_3^{\bullet}$ concentrations at 0.1 M and ca. 0.8 μM in N_2O-saturated aqueous solutions with 5 mM phosphate, pH 7.0, 25 °C.

the pulse radiolytically generated azide radical ($N_3^{\bullet}$).[4] Because the tryptophan (TrpH) side chain has the greater reactivity toward the azide radical, one-electron indole oxidation (eq 1) is the



$$N_3^{\bullet} + \text{TrpH-X-TyrOH} \rightarrow {}^{\bullet}\text{Trp-X-TyrOH} + N_3^- + H^+ \quad (1)$$

predominant reaction of $N_3^{\bullet}$ with peptides that contain both TrpH and TyrOH. As seen in Figure 1, the initial and rapid Trp$^{\bullet}$ formation is followed by the slower intramolecular electron transfer from tyrosine to Trp$^{\bullet}$.

$${}^{\bullet}\text{Trp-X-TyrOH} \rightleftharpoons \text{TrpH-X-TyrO}^{\bullet} \quad (2)$$

Note that after reaction 2 the Trp$^{\bullet}$ absorbance at 510 nm does not return to the base line due to the finite equilibrium position of this reaction.[5] Note also that the electron transfer at pH 7 is accompanied by a proton transfer due to the pK_a of 4.3 and <0 associated with the two cation radicals TrpH$^{\bullet+}$ and TyrOH$^{\bullet+}$, respectively.[6]

Table I. Electron Transfer between Tryptophan and Tyrosine

peptide	k_{intra}, s^{-1}		E_a, KJ/mol	
	this lab[a]	lit.	this lab	lit.
TrpH-TyrOH	7.4 × 10^4 [b]	7.3 × 10^4 [c]		21,[c] 18.7[d]
TrpH-Pro-TyrOH	2.4 × 10^4	2.6 × 10^4 [d]	22	21.1[d]
Lys-TrpH-Pro-TyrOH·Lys	2.4 × 10^4			
TrpH-$(Pro)_2$-TyrOH	0.67 × 10^4 [b]	0.49 × 10^4 [d]	17	18.4[d]
TrpH-$(Pro)_3$-TyrOH	0.23 × 10^4 [b]	0.15 × 10^4 [d]		17.5[d]
TrpH-$(Pro)_4$-TyrOH	0.085 × 10^4			
TrpH-$(Pro)_5$-TyrOH	0.025 × 10^4			
TyrOH-TrpH	6.7 × 10^4 [b]	5.4 × 10^4 [c]	22	
TyrOH-Pro-TrpH	0.72 × 10^4 [b]		27	
Lys-TyrOH-Pro-TrpH-Lys	0.53 × 10^4			
TyrOH-$(Pro)_2$-TrpH	0.32 × 10^4 [b]			
TyrOH-$(Pro)_3$-TrpH	0.20 × 10^4 [b]			
TyrOH-$(Pro)_4$-TrpH	0.086 × 10^4			
TyrOH-$(Pro)_5$-TrpH	0.048 × 10^4			

[a] The estimated errors for these rate constants fall in the range of 10–20%; because of the size of the estimated equilibrium constants, the apparent rate constants are approximately those for the electron transfer from TyrOH to Trp$^{\bullet}$. [b] Reference 4. [c] Prütz, W. A.; Land, E. J.; Sloper, R. W. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 281–292. [d] Reference 9.

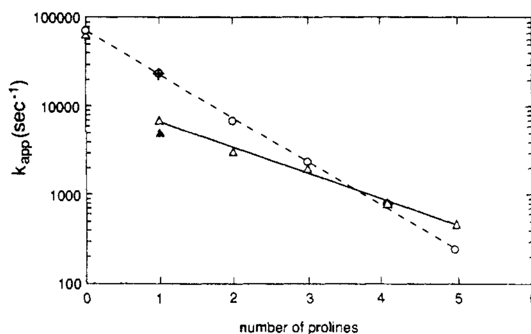


Figure 2. LRET rate constant dependence on peptide chain length. All rate constants were obtained under conditions similar to those given in the caption to Figure 1: O, TrpH-$(Pro)_n$-TyrOH; Δ, TyrOH-$(Pro)_n$-TrpH; +, Lys-TrpH-Pro-TyrOH-Lys; ▲, Lys-TyrOH-Pro-TrpH-Lys.

Oligoproline is particularly appropriate as an LRET spacer since the redox centers at its two ends are held scrupulously apart,[7] and the separation distance increases linearly with each added proline.[8] Thus, oligoproline has been used to separate a variety of redox couples, of which TrpH and TyrOH comprise just one.[4,9,10] In each case the apparent first-order intramolecular rate constant decreases exponentially with increasing distance, as predicted by Marcus theory.[11] However, when Trp$^{\bullet}$ and TyrOH are the redox pair, the magnitude of this exponential dependence is low and apparently sensitive to the amino acid order in the peptide.[4] We now have additional data that verify and expand on these previous results.

We have shown previously[4] that the observed one-step electron transfer (eq 2) is an intramolecular, not intermolecular, process. Those earlier results, the first-order rate constants newly measured for this report, and those activation energies (E_a) obtained to date

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(5) One calculates the redox potential difference $\Delta E'$ from the magnitudes of the equilibrium absorbances (A_∞) at 510 and 410 nm. To correct for a slow radical decay, we extracted A_0, the absorbance at time zero, and A_∞ from the nonlinear least-squares fit of the reaction time course at both 410 and 510 nm to a biexponential function. In one of the three ways in which we computed the equilibrium constant K_{eq}, we obtained the equilibrium concentrations of Trp$^{\bullet}$ ($c^{\infty}_{Trp^{\bullet}}$) and TyrO$^{\bullet}$ ($c^{\infty}_{TyrO^{\bullet}}$) from

$$c^{\infty}_{TyrO^{\bullet}} = \frac{A_{\infty,410}}{\epsilon_{410} l} \qquad c^{\infty}_{Trp^{\bullet}} = \frac{A_{\infty,510}}{\epsilon_{510} l} \qquad K_{eq} = c^{\infty}_{TyrO^{\bullet}}/c^{\infty}_{Trp^{\bullet}}$$

where l is the light path length, ϵ_{510} of Trp$^{\bullet}$ was taken as 1800 M^{-1} cm^{-1}, and ϵ_{410} of TyrO$^{\bullet}$ was taken as 2600 M^{-1} cm^{-1}. (Bensasson, R. V.; Land, E. J.; Truscott, T. G. *Flash Photolysis and Pulse Radiolysis*; Pergamon Press: Oxford, 1983; pp 106.)

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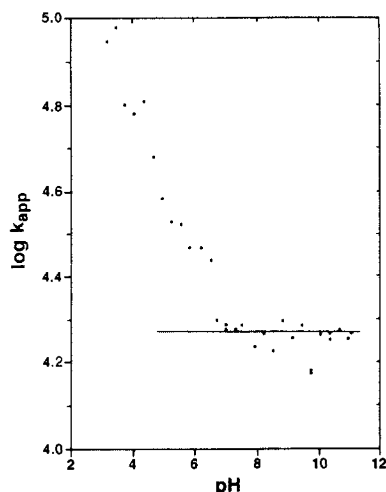

Figure 3. LRET rate constant dependence on pH. Since azide is an acid at low pH, tryptophan oxidation was accomplished with the dibromide radical, $Br_2^{\bullet -}$ formed in the same way as $N_3^{\bullet}$. The solute concentrations were peptide ca. 100 μM, Br^- 0.1 M, and phosphate buffer 5 mM, with all solutions saturated by N_2O and at 25 °C. The concentration of $Br_2^{\bullet -}$ generated by the pulse was 1 μM. The solution pH was adjusted up from pH 7 with N_2O-saturated NaOH, and down from pH 7 with N_2O-saturated HCl. The horizontal line drawn through the points is the average of the included rate constants.

are collected in Table I. As seen in Figure 2, the rate constants for the series TyrOH-$(Pro)_n$-TrpH, with the exception of the dipeptide TyrOH-TrpH, fall off exponentially with distance; the rate constants for the reversed series TrpH-$(Pro)_n$-TyrOH show the same dependence, but with a different apparent slope β. Assuming that each added proline separates the two aromatic amino acids by an additional 3.1 Å, we estimate β values of 0.23 $Å^{-1}$ and 0.37 $Å^{-1}$ for TyrOH-$(Pro)_n$-TrpH and TrpH-$(Pro)_n$-TyrOH, respectively. The result of this difference is a crossover in rate constants; while LRET is faster in TrpH-Pro-TyrOH than in TyrOH-Pro-TrpH, the reverse holds for the longest peptides. Our previous experiments suggest that the redox potential difference, $\Delta E'$, between the $Trp^{\bullet}$/TrpH and the $TyrO^{\bullet}$/TyrOH couples does not change with chain length,[4] eliminating this as a possible explanation of these unique results.

Although there is a net proton transfer in reaction 2, we had argued previously that this proton transfer cannot be rate determining at pH 7.0.[4] We now have additional data to support that kinetic argument: (i) in the TrpH-$(Pro)_n$-TyrOH series the observed rate constant decreases by a factor of approximately 300 from dipeptide to heptapeptide; and (ii) the electron transfer rate in TrpH-Pro-TyrOH is independent of pH from ca. 6.5 to 11 (Figure 3), although k_{app} does increase below 6.[12]

Might a "chain-end" effect explain the observed difference in β? For example, TyrOH and TrpH at the peptide chain ends interact electrostatically with the N-terminal ammonium and C-terminal carboxylate to affect electron transfer differentially. But there is no chain-end effect, for the LRET rate constants are unchanged with lysine addition to both the C- and N-terminal ends of TrpH-Pro-TyrOH and TyrOH-Pro-TrpH (Table I and Figure 2). Our previous conjecture on a correlation between the magnitude of β and the equilibrium redox potential difference, $\Delta E'$, is also inconsistent with these results. From equilibrium absorbances, such as those in Figure 1, we have estimated $\Delta E'$ for Lys-Tyr-Pro-Trp-Lys and Lys-Trp-Pro-Tyr-Lys of 41 and 61 mV, respectively; the same within experimental error.

In the absence of other alternatives, we conclude that just the order of the TyrOH and TrpH residues in the asymmetric polypeptide chain may be responsible for the kinetic differences between the two peptide series. One possibility is based on the presumably limited number of orientations assumed by the TrpH indole side chain.[13] A hindered side chain would result in a geometric change when TrpH is moved between C- and N-terminal locations. Since Sakata et al.[14] have shown that electron-donor and -acceptor orientations can affect LRET rates, any geometric difference could result in "absolute" rate differences. However, insofar as the TrpH indole conformation should be largely insensitive to the number of prolines in the middle of the chain, this argument cannot explain the observed "relative" difference in β. Any other "absolute" effect is ruled out for the same reason. That the direction of electron transfer in both sets of peptides is from the TyrOH to the TrpH side chain is the basis of a second possible explanation. The difference in the magnitude of β may be due simply to the fact that net electron transfer is from N- to C-terminal in one peptide series and C- to N-terminal in the other. If this suggestion of a directional specificity is correct, then it would be reasonable for this LRET to be through-bond, not through-space. With respect to the low values of β reported here, we note the recent suggestion that through-bond processes should be less sensitive to distance than through-space processes.[15]

The observation of LRET in proteins leads to speculation about evolutionary pressures to direct electron transfer along specific paths and between specific protein groups. Currently, there are hints of such LRET specificity.[16] Our results are the first to suggest that molecular ordering might be one mechanism to establish a path specificity. The observation[14] that electron-donor and -acceptor orientations also affect the LRET rate suggests a second mechanism. The physiological significance of either is presently untested.

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Kinetics of a 1,3-CH Carbene Insertion Reaction: *tert*-Butylchlorocarbene

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Last year, intensive activity was focused on the kinetics of *intramolecular* carbene reactions. This attention was largely restricted to the characteristic[1] 1,2-H[2] and 1,2-C[2f,3] shifts (or "insertions") that result in alkene formation. Much of this work depended on laser flash photolysis (LFP) of diazirine precursors to generate the carbenes that were subsequently monitored

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