Femtosecond Dynamics and Electrocatalysis of the Reduction of O₂: Tetraruthenated Cobalt Porphyrins

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Recently we reported the femtosecond dynamics of some porphyrin molecules.[1] These studies elucidated the elementary steps involved in intramolecular relaxation and charge transfer (CT) in cobalt tetraphenylporphyrin (CoTPP) from the porphyrin π (a_{2u}) system to the Co(d_{z^2}). Our interest in the dynamics of intramolecular electron transfer stems from recent studies of cobalt porphyrins that were modified by attachment of Ru(II) or Os(II) complexes to the periphery of the porphyrin ring.[2] These modified cobalt porphyrins exhibit high catalytic activity for the electroreduction of O₂ directly to H₂O, a process that most monomeric cobalt porphyrins are unable to accomplish. The mechanism by which the modified cobalt porphyrins achieve the direct, four-electron reduction of O₂ has been suggested to involve back-bonding interactions among the attached Ru(II) and Os(II) centers, the porphyrin ring, and the Co(II) ion at its center.[2]

In this paper we report the femtosecond, time-resolved dynamics of a series of ruthenated and nonruthenated cobalt porphyrins (Figure 1). There have been a few reports dealing with the relaxation dynamics of simple cobalt porphyrins,[3–6] but none have involved time-domain measurements for ruthenated porphyrins. We focus on the dynamics of intramolecular electron transfer within both types of cobalt porphyrins and the relationship of the dynamics to the electrocatalytic behavior. The electrochemical and spectroscopic experiments were carried out with the molecules of interest (Figure 1); previous studies of ruthenated porphyrins have appeared.[7–11] The femtosecond transient absorption experiments were carried out with ~0.3 mM solutions of the porphyrins prepared in a mixture of ethylene glycol dimethyl ether (DME) and *N,N*-dimethylacetamide (DMA) (1:0.15 V/V).[12a] The experiments were performed using previously described apparatus.[1,12b]

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(12) (a) The porphyrins in Figure 1 were prepared by the procedure given in: Steiger, B.; Anson, F. C. *J. Porphyrins Phthalocyanines* **1999**, in press. Ethylene glycol dimethyl ether (Aldrich, anhydrous, 99.5%) was passed through a column of alumina (Aldrich, activated, basic, Brockmann I) before use. *N,N*-Dimethylacetamide (Aldrich, anhydrous, 99.8%) was used as received. (b) An amplified titanium–sapphire laser system pumping two optical parametric amplifiers (OPAs) provided femtosecond pump and probe pulses with independent wavelength tunability. The pump pulse was tuned to the Q-band absorption of the porphyrin systems under study. The probe pulse was chosen to avoid the strong absorption of the ruthenium (II) center present in **II** and **IV**.
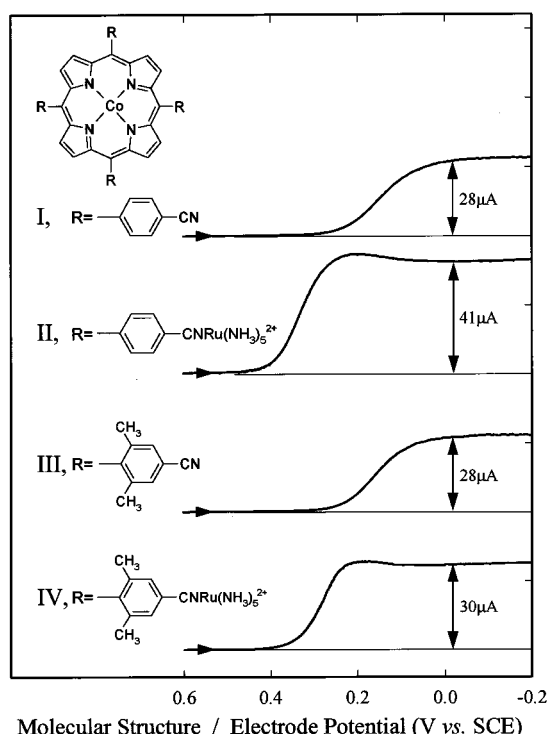

Figure 1. Structures of cobalt(II) porphyrins and reduction of O₂ at a rotating graphite disk electrode coated with the respective porphyrin (~2 × 10⁻⁹ mol·cm⁻²; experimental details are given in ref 13). Note that the four-electron reduction of O₂ produces a significantly larger plateau current for **II** than for **IV** where only a two-electron reduction proceeds. The ratio of the two plateau currents is less than the maximum possible value of 2.0 because of kinetic factors that are explained in refs 2 and 14.

In Figure 2 are shown femtosecond transient absorption profiles of porphyrin molecules **I** to **IV**. The transient absorption profile for **II** exhibits a much slower decay than that for **I**, while the difference between the transients for **III** and **IV** is less dramatic. These data indicate the much stronger influence of ruthenation on the dynamic behavior of **II** compared with that on the behavior of **IV**. The transients in Figure 2 can be fit well using two decay components with different lifetimes and relative amplitudes. The change in lifetime from **I** to **II** is evident, and from the fit we obtained at least a doubling of the values as indicated in Figure 2. Note also that **II** shows a distinct rise time (~300 fs) which was not detected in the other samples.

To confirm that the decay profiles of **II** and **IV** shown in Figure 2 are due to the ruthenated porphyrin systems, two control experiments were carried out. First, a mixture of CoTPP and (benzonitrile)Ru(NH₃)₅²⁺ with a mole ratio of 1:4 was prepared in DME/DMA, and the transient absorption measurements were repeated. The lifetimes and relative amplitude of the transients for CoTPP were essentially unaffected by the presence of the Ru(II) complex. Second, a 1.2 mM solution of the (benzonitrile)-Ru(NH₃)₅²⁺ complex in DME/DMA was examined. It produced insignificant transient absorption.

The relaxation and ligand-to-metal charge separation is accounted for using the following scheme[1]: $^2Q(\pi, \pi^*) \rightarrow {}^2T(\pi, \pi^*) \rightarrow {}^2CT(\pi, d_{z^2}) \rightarrow {}^2T$(ground state). The appearance in the measured transients of contributions from each state depends on the probe wavelength and the specific energetics of the system.[1,3] As shown in ref 1, relaxation in the porphyrin π system takes a few hundred femtoseconds. The absorption assigned to the ²Q state becomes weaker as the wavelength is increased. The absence
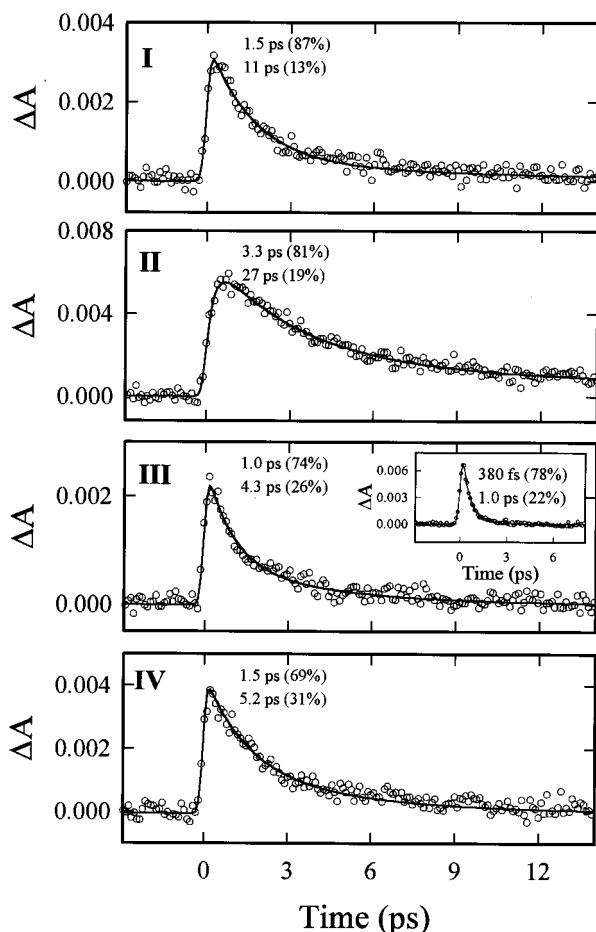
Figure 2. Femtosecond transient absorbance of porphyrins **I** to **IV** in DME/DMA. Pump wavelength, 530 nm; probe wavelength, 610 nm. The insert shows the transient absorption decay profile of **III** when probing at 478 nm. The values given in the figure are lifetimes and relative amplitudes, which are accurate to roughly ±20%.

of a femtosecond dynamic component in **I**, **III**, and **IV** (the result of equal absorbances of the ^2Q and ^2T states, i.e., $A_Q \approx A_T$), and the femtosecond rise in **II** ($A_Q < A_T$), are consistent with this wavelength dependence (see also the insert in Figure 2). The two decay lifetimes listed in Figure 2 are accordingly associated with the sequential creation and decay of the CT state. The large difference in the decay lifetimes of **I** and **II** indicates that both the charge separation and the recombination process are significantly slower for **II** than for **I** while those for **IV** and **III** are similar. The only structural difference between **IV** and **II,** the two methyl groups that force the phenyl group to be more orthogonal to the porphyrin ring in **IV**, apparently dominates the electronic interaction between the coordinated $Ru(NH_3)_5^{2+}$ complexes and the porphyrin ring.

It is striking that the differences in the CT state dynamics of this series of molecules parallel the differences in their electro-

catalytic properties (in their ground states). In particular, converting **I** into **II** by ruthenation converts it from a two- into a four-electron electrocatalyst for the reduction of O_2 (Figure 1) while the same transformation of **III** into **IV** produces no comparable enhancement in current.[2,13] The difference in electrocatalytic activity of **II** and **IV** has been attributed to the diminished transfer of electron density (arising from π-back-bonding by the Ru(II) center) from the phenyl to the porphyrin ring of **IV** compared to **II** because of the increase in the ring-to-ring dihedral angle produced by the methyl groups in **IV**. Recent studies by Bocian et al.[15-17] support this line of reasoning.

The charge transfer studied here is that of the porphyrin ligand to Co(II), resulting in the generation of the porphyrin cation radical and Co(I). The CT state dynamics, therefore, map the extent of the coupling between the π system and the cobalt cation, the center which is key in the catalytic activity toward O_2 (which involves d-π charge transfer from cobalt to O_2 in the transition state). That ruthenation of **I** more than doubles the recombination time of the product (**II**) while ruthenation of **III** affects that of **IV** only slightly, indicates that the back-transfer from Co(I) to the π system is strongly influenced by the presence of the ruthenium complex only when the phenyl ring to which it is coordinated and the porphyrin ring are in conjugation. This feature is entirely consistent with the catalytic influence of the Ru(II) complex as it back-bonds into the π system which, in turn, helps the cobalt center weaken the O−O bond via d-π charge transfer. In the femtosecond measurements, the back-bonding by the Ru(II) center apparently impedes the back-transfer. The parallelism is remarkably consistent in the series studied.

With the above in mind, the observed conjugation-dependent decrease in the rates of the initial charge separation and the subsequent recombination both arise from back-bonding, and it is interesting to consider its possible role in the mechanism. The absorption spectra of the ruthenated and nonruthenated species are similar, indicating that there are no significant changes in the separation of HOMO/LUMO energies. However, the back-bonding in the conjugated system may induce a resonance interaction between ruthenium and the porphyrin system which could influence the charge density around the cobalt center, affecting the energy of the CT state and, therefore, the rates of its formation and decay. The correlation between electrocatalytic activity and the dynamics of the CT state of cobalt porphyrins suggests that there may exist a fundamental link between the two. A search for similar correlations in other electrocatalysts is the object of continuing studies.

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