Femtosecond Dynamics of Dioxygen – Picket-Fence Cobalt Porphyrins: Ultrafast Release of O_2 and the Nature of Dative Bonding**

Beat Steiger, J. Spencer Baskin, Fred C. Anson, and Ahmed H. Zewail*

The natural systems of hemoglobin and myoglobin form reversible complexes with O_2, which are involved in the transport of O_2 in biological systems. The protein environment surrounding the metal center in these molecules controls the rate of the binding of O_2 and discriminates against poisonous carbon monoxide. Synthetic models of these systems have been designed to optimize the binding of O_2 and include "picket-fence", "pocket", "basket-handle", "picnic-basket", and "capped" porphyrins.[1] These models are attractive systems for study because of their high affinities for O_2 at room temperature. Among the issues that can be addressed with these model systems are: 1) the nature of the elementary steps involved in the reactions of O_2 complexes, 2) the influence of hydrogen bonding on the rates of O_2 binding and release, and 3) the geometry of the O_2–metal complex on the time scale of the dynamics.

Herein we report our first study of the femtosecond dynamics of a) a four-coordinate picket-fence cobalt(II) porphyrin in benzene at room temperature, b) its five-coordinate 1-methylimidazole (1-MeIm) adduct (used to enhance the binding of O_2), and c) the six-coordinate O_2 complex of the 1-MeIm adduct (Figure 1). The transient behavior of the two O_2-free porphyrins is very similar to that for cobalt(II) tetraphenylporphyrin. However, a dramatic change in the transient absorption is observed when the porphyrin is oxygenated. These observations indicate the release of the bound O_2 from the active binding site with a total reaction time of 1.9 ± 0.4 ps. We relate such behavior to the nature of the dative cobalt–O_2 bond and the charge redistribution triggered by the direct femtosecond excitation of the complex to the transition state for O_2 release.

In a recent publication[2] we reported a correlation between the electrocatalytic activity of tetraruthenated cobalt porphyrins toward the reduction of O_2[3, 4] and the femtosecond dynamics of their charge transfer states. We have also investigated the femtosecond dynamics of cobalt(II) tetraphenylporphyrin ($Co^{II}TPP$).[5] We were drawn to investigate the dynamics of oxygenated cobalt porphyrins since the cobalt center plays a key role in the catalyzed reduction of O_2. The coordination of O_2 to most four-coordinate cobalt(II) porphyrins or five-coordinate amine adducts of cobalt(II) porphyrins is not favorable at room temperature. It has been estimated for the 1-methylimidazole adduct of cobalt(II) tetra(p-methoxyphenyl)porphyrin that only about 0.8% of the cobalt centers would have O_2 as a sixth ligand in toluene solutions saturated with air.[6] Although more elaborate types of porphyrins exhibit higher affinities for O_2[1, 7] we were attracted to the original picket-fence cobalt porphyrin (Figures 1 and 2) because its structure is relatively close to our previously examined cobalt tetraphenylporphyrins, it binds O_2 with high affinity at room temperature, and the binding is reversible.

The steady-state absorption spectra of the oxygenated and deoxygenated picket-fence cobalt porphyrin (CoP) are differ-

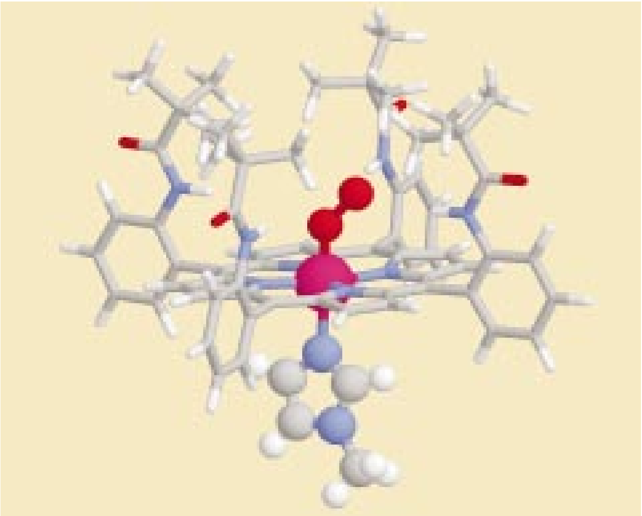

Figure 1. Structural model of the six-coordinate picket-fence cobalt(II) porphyrin examined in this study.

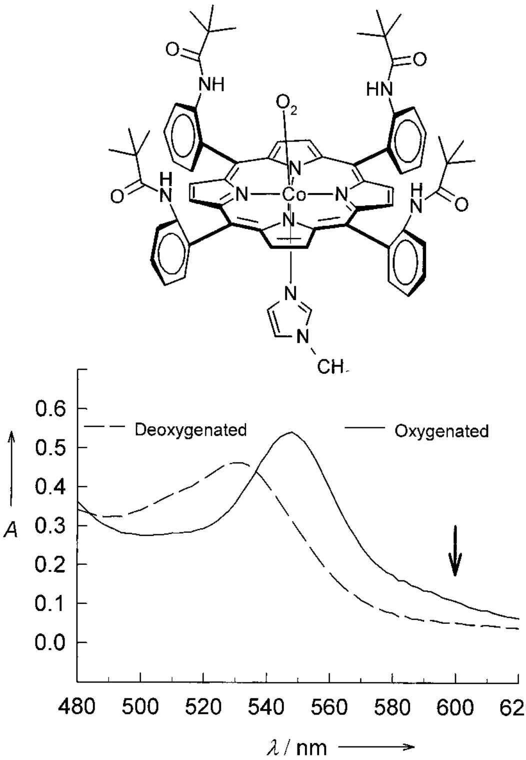

Figure 2. Top: Molecular structure of the model in Figure 1. Bottom: Steady-state absorption spectra of (1-MeIm)–Co^{II}TpivPP in benzene at room temperature: Solutions were equilibrated with 1 atm of argon (dashed curve) or O_2 (solid curve).

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[*] Prof. A. H. Zewail, Dr. B. Steiger, Dr. J. S. Baskin, Prof. F. C. Anson
Laboratory for Molecular Sciences
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, CA 91125 (USA)
Fax: (+1) 626-796-8315
E-mail: zewail@its.caltech.edu

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ent in that the oxygenated form shows a definite red shift at room temperature (Figure 2). A series of transient absorption measurements using a pump wavelength of 545 nm and a probe wavelength of 600 nm is shown in Figure 3. The upper trace in Figure 3A is the transient absorption of CoP in benzene at room temperature under 1 atm of argon. The temporal evolution is very similar to that reported previously for Co^{II}TPP.[5] It consists of three exponential decay components (having relative amplitudes of 57%, 34%, and 9%, respectively) with lifetimes indicated in the figure. The measurement was repeated in the presence of 4 mM 1-MeIm (referred to as base, B), which converts more than 98% of the porphyrin into five-coordinate B-CoP,[8] and resulted in the generation of the second trace in Figure 3A. Although the lifetimes are somewhat shortened, and the relative amplitudes change, the three decay components are still present.

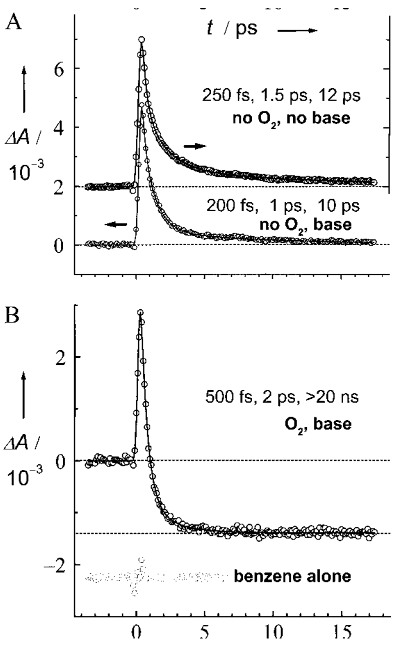

Figure 3. Femtosecond transient absorption at 600 nm of picket-fence cobalt porphyrin in benzene with excitation at 545 nm. A) Transients measured under argon, with and without complexation by (4 mM) 1-MeIm (base); B) Transient measured in 4 mM 1-MeIm under 1 atm of O_2, and the transient for pure benzene.

Figure 3B shows the response obtained after the B-CoP + 4 mM 1-MeIm solution was saturated with O_2, which converts approximately 85% of the porphyrin into B-CoP-O_2.[9] Since the absorbance of B-CoP-O_2 at 545 nm is higher than that of B-CoP (see Figure 2), we estimate that about 90% of the photoexcited porphyrin contains coordinated O_2. The presence of O_2 causes a dramatic change in the transient behavior: following the absorbance increase at $t = 0$, there is a substantial bleaching, or decrease in absorbance, at longer times. The long-lived plateau of the bleaching signal is reached within 4 to 5 ps. This plateau does not decay appreciably over the maximum range of our delay time, which indicates a recovery lifetime of at least 20 ns. (A slight ($<10\%$) decrease in this plateau level appears to occur on a time scale of tens of picoseconds).

We performed similar experiments probing at 471 nm. In the absence of O_2 the longest component (with a 10 to 20 ps lifetime) was relatively weak compared to that at 600 nm, which matched the trend observed for Co^{II}TPP.[5] In the presence of O_2 the 471 nm transient was dominated by a 200 fs decay component followed by a long-lived negative plateau similar to that at 600 nm. However, the response was complicated by at least three additional relaxation components. The measurements at 600 nm are unique because they probe only the tail of the Q-band absorption (see Figure 2).

Hoshino concluded from the transient absorption spectrum of CoTPP-O_2 in O_2-saturated 2-methyltetrahydrofuran at low temperature (140–200 K)[10] that the product detected on the nanosecond time scale (following photolysis at 532 nm) was *ground-state* Co^{II}TPP, which subsequently recombined (nongeminately) with O_2 on the microsecond time scale. Similarly, in our experiments B-CoP is produced at long times in its ground state. A negative change in the transient absorption at 600 nm, as seen in the transient shown in Figure 3B, is then predicted because the B-CoP complex absorbs only weakly at 600 nm (Figure 2). Lending further support to this assignment of the product is the fact that the spectrum and transient behavior observed prior to the addition of O_2 were fully recovered when the same sample was again placed under argon, which demonstrated that no significant oxidation or other degradation of the porphyrin sample had occurred during the experiments under O_2 saturation.

The fact that the 600 nm absorbance does not recover appreciably on the nanosecond time scale shows that the extent of geminate recombination of O_2 and B-CoP is small. This behavior contrasts with the 43% recombination efficiency reported for O_2 and picket-fence iron porphyrin, B-FeP (B = 1-MeIm), in toluene with excitation at 314 nm.[11] It is interesting to note that the photoinduced release of CO from myoglobin is characterized by an absence of geminate recombination.[12] In that case the direct monitoring of the CO has shown that it is released from the metal coordination site and trapped in a pocket of the heme protein within 500 fs. The protein environment surrounding the trapping site then undergoes relaxation with a time constant of 1.6 ps.[13] However, it is not necessary to invoke such a trapping mechanism in all cases of low geminate recombination since ligand–porphyrin association rates depend strongly on the specific ligand and metal center. The contrast in the geminate recombination of O_2 with B-CoP and B-FeP is consistent with the smaller equilibrium binding of O_2 with B-CoP.[14, 15]

The nature of the ultrafast dynamics of the O_2 release can now be addressed. The first steps parallel those previously deduced for CoTPP.[5, 16] Relaxation within the porphyrin system (200 fs, prominent only when probing at 471 nm) precedes porphyrin-to-metal electron-transfer, but the latter occurs at an enhanced rate (500 fs as opposed to 1–2 ps) because of the dative bonding of cobalt and O_2, as discussed below. (The absence of a clear 200 fs component at 600 nm is understandable because the 600 nm probe is expected to be less sensitive to the initial state than is the 471 nm probe.[5]) The strong O_2 bonding in the adduct ground state ($\Delta H = -12.2\ \mathrm{kcal\,mol^{-1}}$)[14] has significant Co^{III}-O_2^- character and is made possible only through the influence of the base on the metal center; the behavior of the transient profile seen in Figure 3A shows that the perturbation of the porphyrin system by the base alone is not severe.

The dative bonding of O_2 to cobalt depends critically on the interaction of the d_{z^2} orbital on Co with the π^* orbital on O_2 (through a σ-type interaction) and on the back-bonding from the metal d-π orbitals to O_2. The noncolinear configuration enhances the σ-bonding, and, because the d_{z^2} electron of Co is engaged in bonding, the oxidation state of Co approaches +3.[17, 18, 19] Following femtosecond excitation the charge transfer from the porphyrin-based π system to the base-metal-O_2 system restores an electron to the cobalt d_{z^2} orbital and weakens the metal-O_2 bond. Reverse charge transfer and release of the O_2 can then occur in concert to produce the free porphyrin in its ground state in 2 ps. That this process occurs faster than the 10 ps decay of the charge-transfer state in the absence of oxygen (Figure 3A) may be related to the different natures of the charge-transfer state with and without O_2. The porphyrin-to-metal charge-transfer state of B-CoP has a measurable absorption at 600 nm as evidenced by the 10 ps component in Figure 3A. The fact that no 10 ps decay component appears in the transient of B-CoP-O_2 means that B-CoP was not formed in the excited state, and thus confirms that release of O_2 directly produces the B-CoP complex in its ground state.[20]

The total reaction time is 2 ps. In general, the release of O_2 involves the breakage of the bond and the reorganization around the active site, as discussed for myoglobin–CO.[13] It should be noted that the dative character of the bond could lead to two different channels: either homolytic cleavage to release O_2 or heterolytic cleavage to form superoxide. Our results, as in the case of ref. [10], support the homolytic channel: the ground state of B-CoP is $d_{z^2}^1$, similar to the CT state of B-CoP-O_2, while the ground state of the latter is essentially $d_{z^2}^0$. Our findings may be relevant to other recent studies, including a report of the photoejection of O_2 in less than 2 ps from an oxygenated Co^{II}porphyrin–Al^{III}phthalocyanine aggregate[21] and studies on oxyhemoproteins (oxyhemoglobin, oxymyoglobin, etc.) in fast spectroscopic experiments by Petrich et al.,[22] and others, as summarized by Šima.[23]

In conclusion, excitation of the O_2 adduct of the picket-fence porphyrin within the Q-band leads to ultrafast (2 ps) ejection of O_2, which is a reflection of the influence of charge redistribution within the complex on the O_2-Co dative bond. The entry to the transition state of these systems allows us to study the direct evolution to products and to dissect the elementary steps, similar to what has been achieved in elementary charge-transfer systems.[24] There is a host of additional experiments to be carried out on these novel models.

Experimental Section

Our laser system has been described in detail elsewhere.[5] Basically, an amplified 790 nm pulse train (1.8 W, 1 kHz) from a Ti/Sapphire laser was used to pump two optical parametric amplifiers to produce independently tunable pump and probe beams. The pump beam was directed through a variable delay line and a beam chopper and overlapped with the probe beam in a 1 mm path-length glass cell containing the sample solution. The polarization and power of both beams were adjusted as required (pump power 2 μJ, probe power 50 nJ, magic angle probing), lightly focused (spot size ca. 0.5 mm), and crossed at a small angle (ca. 2°). The probe power was detected after the cell by a photodiode and the gated and integrated signal was normalized to a similarly processed signal from a photodiode sampling the probe power before the cell. The change in absorbance was obtained from the signals with and without pump excitation as determined by the chopper. The total temporal response of the experiments was determined to be 300–350 fs full width at half maximum height.

The picket-fence free base porphyrin, 5,10,15,20-tetrakis($\alpha,\alpha,\alpha,\alpha$-2-pivalamido-phenyl)porphyrin ($\alpha,\alpha,\alpha,\alpha$-$H_2$TpivPP), was synthesized by first preparing the 5,10,15,20-tetrakis(2-nitrophenyl)porphyrin in 11% yield by condensing 2-nitrobenzaldehyde with pyrrole in boiling glacial acetic acid according to the procedure of Collman et al.[25] The crude product was used as obtained in the further reaction in which the nitro groups were converted into the amines by reduction with excess $SnCl_2$ in concentrated HCl at 65–70 °C.[25] The crystalline product, 5,10,15,20-tetrakis(2-aminophenyl)porphyrin (H_2TamPP), isolated in 92% yield, was a mixture of the four atropisomers in statistical abundance ($\alpha,\beta,\alpha,\beta$-:$\alpha,\alpha,\beta,\beta$-:$\alpha,\alpha,\alpha,\beta$-:$\alpha,\alpha,\alpha,\alpha$-atropisomer = 1:2:4:1), as indicated by thin layer chromatography on silica gel with benzene:diethyl ether (1:1). The $\alpha,\alpha,\alpha,\alpha$-atropisomer was obtained in 60% yield by conversion of the random mixture of atropisomers by the silica gel/benzene reflux method,[26] followed by purification by column chromatography and crystallization from $CHCl_3$/MeOH mixtures. The 500 MHz ^{1}H NMR and UV/Vis spectra of $\alpha,\alpha,\alpha,\alpha$-$H_2$TamPP were in agreement with those previously reported.[26]

$\alpha,\alpha,\alpha,\alpha$-$H_2$TamPP was reacted with pivaloyl chloride and the product was purified by column chromatography on silica gel followed by recrystallization from a $CHCl_3$/EtOH/heptane mixture to give pure $\alpha,\alpha,\alpha,\alpha$-$H_2$TpivPP, as confirmed by the 500 MHz ^{1}H NMR and UV/Vis spectra. The picket-fence cobalt(II) porphyrin, [5,10,15,20-tetrakis($\alpha,\alpha,\alpha,\alpha$-2-pivalamidophenyl)porphyrinato]cobalt(II) (Co^{II}TpivPP), was prepared by heating a solution of $\alpha,\alpha,\alpha,\alpha$-$H_2$TpivPP in THF at 50 °C for 2 h with excess anhydrous $CoCl_2$ and 2,6-lutidine.[14] The product was purified by chromatography on alumina followed by crystallization from benzene. The 500 MHz ^{1}H NMR and UV/Vis spectra of $\alpha,\alpha,\alpha,\alpha$-$Co^{II}$TpivPP were in agreement with those previously reported.[14, 27]. The photo- and thermal isomerization of several picket-fence systems have been studied.[28] The thermal process is negligible at room temperature and the photochemical process occurs only in long-lived triplet states with very low yields; unlike these systems, Co^{II}TpivPP has an ultrashort excited state lifetime.

Typically, we performed a sequence of four femtosecond transient absorption measurements. We first measured the transient absorption of Co^{II}TpivPP in benzene, freshly passed through a column of alumina, at room temperature and under 1 atm of argon in a 1 mm path-length glass cell (with reservoir, hi-vac valve, and a 24/40 joint adapter closed with septum); the concentration of the porphyrin was adjusted to yield a static absorbance of about 0.2 at 550 nm. 1-Methylimidazole (redistilled) was subsequently added, still under 1 atm of argon, to produce a 4 mM solution. The visible absorption spectrum showed bands at 508 and 530 nm. The transient absorption measurement was then repeated. For the next experiments, O_2 at 1 atm was bubbled through the solution at room temperature until the absorption band at 548 nm (B-CoP-O_2) showed no further change. Preparation of the sample for the final run involved bubbling argon through the solution until the visible absorption spectrum for B-CoP was recovered.

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Femtosecond Dynamics of Norrish Type-II Reactions: Nonconcerted Hydrogen-Transfer and Diradical Intermediacy[**]

Steven De Feyter, Eric W.-G. Diau, and
Ahmed H. Zewail[*]

Herein we report our first real-time study of the dynamics of Norrish type-II reactions: the intramolecular hydrogen transfer and the reaction of the intermediate, diradical species. The nuclear motions associated with the breakage of C–H and C–C bonds and formation of O–H and C–C bonds are studied for the series 2-pentanone, 2-hexanone, and 5-methyl-2-hexanone, using femtosecond time-resolved mass spectrometry. The time scale for the ultrafast hydrogen atom transfer (70–90 fs) and diradical closure and cleavage (400–700 fs) are obtained from the time evolution of the mass-gated species—the observed and vastly different reaction times indicate the nonconcerted nature of the two steps. Density functional theory (DFT) calculations are also reported to elucidate the energetics along the reaction path, and we address the analogy with the McLafferty rearrangement in ion chemistry.

Norrish type-I[1] and type-II[2] reactions are of fundamental importance in photochemistry. The contrast between photochemical and thermal reactions of ketones has been of interest for more than 50 years. Elsewhere, the femtosecond (fs) dynamics of Norrish type-I reactions have been reported.[3,4] In these reactions the α-cleavage is the pathway for product formation. In contrast, in Norrish type-II reactions carbonyl compounds containing γ C–H bonds undergo a 1,5-hydrogen shift upon electronic excitation and yield new products by cleavage and cyclization processes. Figure 1 lists the molecular structures of the systems studied here; three have γ C–H bonds and for calibration purposes one does not.

The literature is rich with detailed studies in the solution and gas phases, with primary focus on the photochemistry of the first excited S_1 state.[2] As noted in these studies the Norrish type-II reaction is deduced, from yield and quenching experiments, to be on the nanosecond time scale and competes with vibrational relaxation and intersystem crossing; there is a barrier for excited singlet reactions of about $4\,\mathrm{kcal\,mol^{-1}}$. The studies reported here are at higher energy (see Figure 2) and are designed to address the primary ultrafast dynamics without complications from much slower relaxation processes. However, the Norrish type-II elementary processes discussed here are the two described in ref. [2] for the overall mechanism.

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[*] Prof. A. H. Zewail, Dr. S. De Feyter, Dr. E. W.-G. Diau
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, CA 91125 (USA)
Fax: (+1) 626-792-8456
E-mail: zewail@caltech.edu

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