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Light Triggered Dioxygen Complexation by Co^{II}-*meso*-tetraphenylporphyrin and Long Chain Derivatives in Aqueous Micellar Solutions

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The complexation of dioxygen, triggered by a photodeligandation of Co(II)TPP and long chain substituted derivatives, is shown to be a general reaction in aqueous micellar solutions. A very interesting feature exhibited by some of these systems is the room temperature reversibility of dioxygen complexation even in dilute solutions of a detergent in water. Dioxygen binding is induced by irradiation in the Soret band as well as in the visible absorption band. An explanation of this reaction, based on the initial binding on the fifth and sixth axial co-ordination sites of the cobalt atom, of either an ether oxygen of Triton or of a water molecule, or of both of them, is proposed. Visible irradiation would eject one of these ligands, leaving room for an incoming dioxygen. It is also shown that although these results may explain the mechanism, other elements are needed to explain the stability and the reversibility of these systems. In this respect, it is shown that the existence of a liquid interface, with its directional and polar character, is essential. Other regioselective interactions between solvent molecules, or specific parts of the detergent molecule, and the cobalt porphyrins come into play. Quantum yields for the photoprocesses and thermodynamic data are given for ionic and non-ionic micellar solutions.

These results show that most of the conditions required for cobalt-reconstituted biological dioxygen carriers to be as functional as natural carriers, can be met in some of these simple models.

In micellar organized media, the simultaneous presence of separated aqueous and hydrocarbon-like phases and the specific properties of their common interface have stimulated a large amount of work.[1] As part of our continuing interest in the understanding of thermal and photochemical reactivity in organized media,[2] we decided to probe the behaviour of simple dioxygen carriers. In this respect, naturally included in the specific properties of micellar solutions, one finds two of the most desired features: the presence of hydrophobic pockets of roughly molecular size[3] and the ability to isolate spatially individual molecules.[4]

Modelling of dioxygen transport and catalysed hydroxylation has mostly drawn on the common features of natural metallo-proteins, whether they belong to haemoglobin and its analogues[5] or to the cytochrome P-450 and cytochrome C oxidase family:[6] the key building block is an Fe-porphyrinic macrocycle.[7] Nevertheless, early results on synthetic dioxygen carriers were obtained with Co instead of Fe complexes,[8,9] and were followed by preparation of a reversible 1:1 macrocyclic complex in organic solution.[10,11] At that stage, interest shifted to Co porphyrins, mostly in toluene at low temperature and in the presence of a co-ordinating base.[12–15] In contrast with natural and reconstituted biological carriers, simple metalloporphyrins show very little tendency to bind dioxygen in solutions at room temperature, which indicates that the environment provided by the protein plays a major role. These dioxygen complexations are usually described by equations (1)–(5)[15b] where P stands for porphyrin, M for the Co or Fe metal

$$\mathrm{MP + B \rightleftharpoons MPB} \qquad (1)$$

$$\mathrm{MPB + O_2 \rightleftharpoons MPB(O_2)} \qquad (2)$$

$$\mathrm{MPB(O_2) + MPB \longrightarrow MPB(O_2)MPB} \qquad (3)$$

$$\mathrm{MPB(O_2)MPB \longrightarrow autoxidation}^{16,17} \qquad (4)$$

$$\mathrm{MPB + B \rightleftharpoons MPB_2} \qquad (5)$$

atom, and B for an organic base. Equation (3) represents an irreversible step corresponding to the formation of a μ-peroxo compound which leads in its turn to autoxidation products.[16,17] Dioxygen-carriers were also prepared using a variety of hindered iron and cobalt porphyrins to avoid step (3), which requires free access to the O_2 moiety of MPB(O_2) by MPB in a diffusion-controlled process. Some of these elaborate molecules are good reversible carriers in organic solvents.[15b,18] and so we decided to look at the behaviour of simple Co^{II}-*meso*-tetraphenylporphyrins† in micellar solutions (Figure 1). In this paper, it is shown that in aqueous non-ionic and ionic micellar solutions, these metallo-porphyrins bind dioxygen at room temperature. This binding is very often reversible. It is also shown that, aside from the usual spontaneous ground-state complexation which is observed for many metallo-porphyrin/detergent couples, there exists a dioxygen complexation triggered by a photodeligandation which is effective for all metalloporphyrin/detergent couples. A careful analysis of this new reaction favours ligand photodissociation as the initial step. It also leads to the conclusion that if the gross features of these processes are the same, the binding parameters of dioxygen are exceptionally sensitive to structural and environmental modifications of the metalloporphyrins.

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† The following abbreviations will be used: TPP stands for the dianion of *meso*-tetraphenylporphyrin, where TPP(1) and TPP(4) refer to TPP substituted in only one or on all four rings, in an *ortho* position, by a hydroxy group *O*-alkylated by an n-hexadecyl chain, respectively. B represents any neutral ligand which could bind to the Co atom in an axial position.

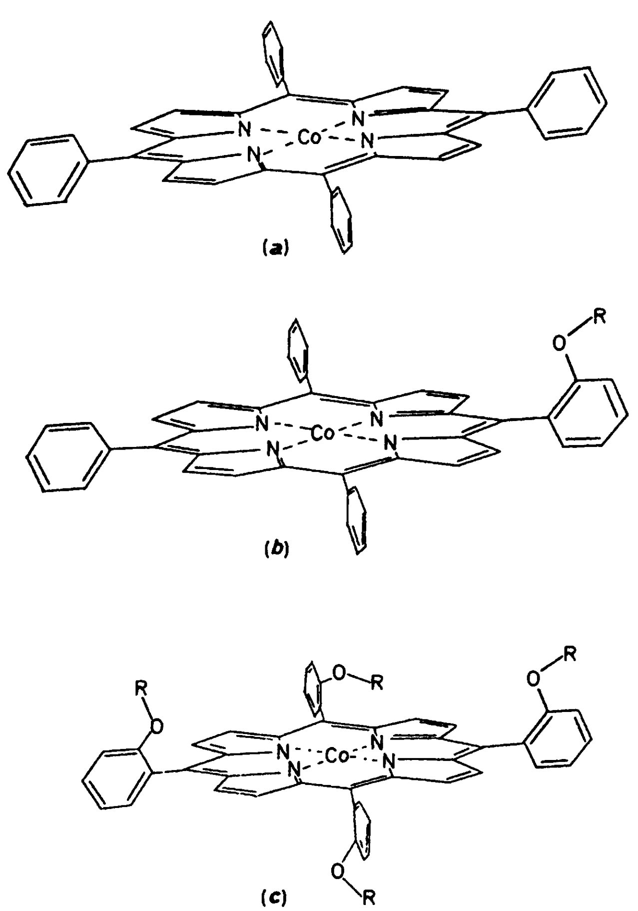


Figure 1. Structures of the Co^{II}-*mesa*-tetraphenylporphyrins (see footnote page 1105): (*a*), (*b*), and (*c*) represent, respectively, Co^{II}TPP, Co^{II}TPP(1), and Co^{II}TPP(4) and R an n-hexadecyl alkyl chain.

Table 1. Wavelength of maximum absorbance at the Soret and visible bands in aqueous micellar solution of Triton X-100.

	Soret/nm		Visible/nm	
Compound	I[a]	II[b]	I[a]	II[b]
Co^{II}TTP	410	430	525	545
Co^{II}TPPB	410	432	525	545
Co^{II}TPP(1)	411	431	530	550
Co^{II}TPP(1)B	411	432	530	550
Co^{II}TPP(4)	410	430	530	550
Co^{II}TPP(4)B	411	432	530	550

B refers to pyridine bound in an axial position. [a] Porphyrin not complexed to dioxygen. [b] Porphyrin complexed to dioxygen.

Results

*Triton X-*100 *Solutions*.—The behaviour of the simplest porphyrin, Co^{II}TPP, will be given first. Co^{II}TPP has a very low solubility in water ($< 10^{-8}$ mol dm^{-3}) but in micellar solutions of Triton X-100, concentrations of 10^{-6} mol dm^{-3} to 10^{-5} mol dm^{-3} were obtained. We kept the detergent concentration equal to or lower than five times the critical micelle concentration (cmc) to ensure nearly spherical micelles, which can be considered as non-interacting.[19] For Co^{II}TPP, compared with what we observed in ionic detergents, solubilization in Triton X-100 is more efficient, probably due to specific interaction between the phenyl rings of the porphyrin and the detergent. Such aerated solutions, kept at room temperature in the dark are stable for several months, and show a Soret band at 410 nm and a visible band at 525 nm (Table 1), indicating that no spontaneous dioxygen complexation is observed under these conditions. However, broadband irradiation with visible light from the sun or from a tungsten lamp brings about a continuous change in the absorption spectrum: both the Soret band and the visible band disappear and are gradually replaced by two new bands at 430 and 550 nm, respectively. This conversion can be brought to completion in 1–3 h, depending on the irradiation conditions (Figure 2), and the absorbance of the peak at 430 nm then matches exactly the initial absorbance at 410 nm of the unirradiated sample. Isosbestic points are observed at 415 and 520 nm in the time dependant spectra of the irradiated solutions. As we have shown in a preliminary study,[20] as soon as irradiation is stopped, the reverse process takes place. In the dark, the latter occurs with a clean first-order rate constant of 5×10^{-5} s^{-1} at 25 °C. The reversibility is total if one waits long enough (Figure 2). In this way, the system can be cycled several times and up to 9 complete cycles have been carried out without degradation.

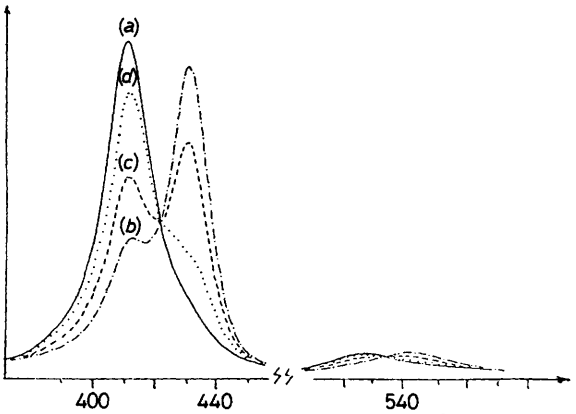


Figure 2. Evolution of the absorption spectrum of Co^{II}TPP in Triton X-100 micellar solutions: (*a*), solution kept in the dark; (*b*), after 2 h irradiation at 410 nm; (*c*), partial recovery after 4 h in the dark; (*d*) near end of recovery after the sixth light–darkness cycle is completed.

These spectral changes, which occur on irradiation, are not observed in carefully degassed solutions and are identical with those which appear in the absorption spectra of Co^{II}–protoporphyrin-IX dimethyl ester in aerated toluene at low temperature[21,14b] and cobalt 'picket fence' porphyrins at room temperature[18b,e] during dioxygen complexation. Furthermore, the UV spectra of the irradiated samples show absorption maxima at the same wavelength as complexes of general formula ROO-Co^{II}TPP where the peroxyalkyl ligand is in the axial position. The latter were obtained by light exposure of various alkyl (tetraporphyrinato-Co^{II}) compounds in oxygen saturated solutions.[22]

ESR spectra of these micellar solutions were taken in the following conditions. After visible irradiation, samples were briefly flushed with pure argon and quickly cooled to 120 K. The spectra obtained (Figure 3) reveal a mixture of Co^{II}TPP and a new species. For the former, the values are $g_{\perp} = 2.5041$ and $g_{\parallel} = 1.9478 \pm 0.0004$ with $A_{\perp} = 114$ and $A_{\parallel} = 91 \pm 0.5$ G, respectively, corresponding to a low-spin configuration with a single electron in a d_{z^2} orbital, whereas in the latter, a signal at $g_{iso} = 2.0560 \pm 0.0003$ corresponds to the cobalt porphyrin complexed to dioxygen.[7e,15b,21,22b,23] This signal is due to a single electron mostly localized in a π-antibonding orbital of dioxygen, and the formula of such a species is often represented[23a] by Co^{III}–O–O$\cdot^{-}$.

These experimental results point to a number of interesting features. The first observation relates to the irradiation-dependent dioxygen complexation. In the photochemistry of

Table 2. Quantum yields for the complexation of dioxygen triggered by photodeligandation and for its photodissociation in Triton X-100 solutions, at room temperature (values ± 10%).

	Complexation ($10^3\varphi$)	Dissociation ($10^3\varphi$)
$Co^{II}TPP$	3.76	0.51[a]
$Co^{II}TPPB$	51	0.58[a]
$Co^{II}TPP(1)$	0.21	0.18[a]
$Co^{II}TPP(1)B$	1.92	0.21[a]
$Co^{II}TPP(4)$	2.86	2.15
$Co^{II}TPP(4)B$	5.50	2.0

[a] Solutions of the oxygenated complexes sealed under vacuum before irradiation.

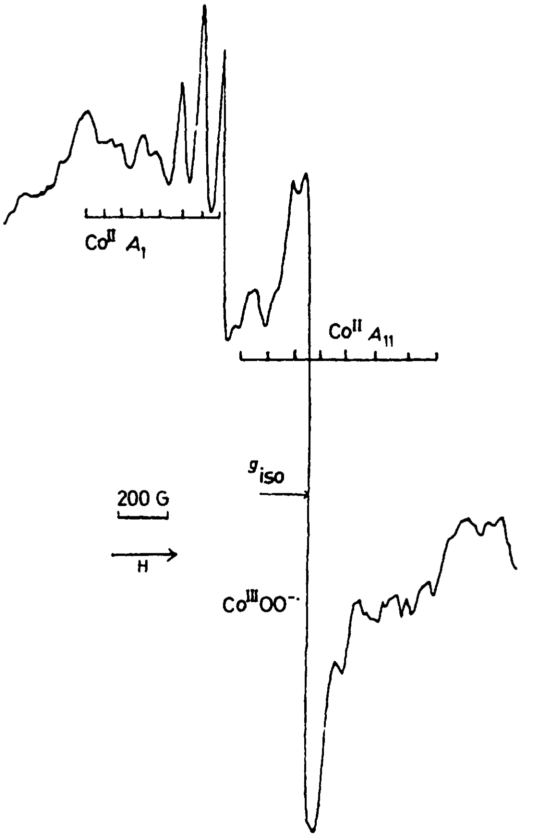


Figure 3. ESR spectrum of $Co^{II}TPP$ in a solution of Triton X-100 at 120 K, after four accumulations (signal gain 6.3 × 10^5, modulation frequency 100 KHz, power 200 mW).

metal complexes, photoelimination of molecules like CO, N_2, or O_2 is well known[24–26] but we are not aware of an example of the reverse process. To understand this new reaction we need to look at the environment of the Co atom in molecules solubilized in an aqueous medium. It is known that H_2O may be complexed to Co atoms in chemically related macrocyclic complexes.[7a] Furthermore, efficient dioxygen complexation in artificial carriers is always obtained in the presence of an added organic base.[7,12–15] We think that in the absence of the latter, the Co atom is complexed to H_2O or to the O atom of the ether group present in Triton X-100 or to both, and that the primary photochemical event is the photodissociation of one of these bound ligands. Competition between dioxygen and one of these unbound ligands to fill a vacant position on Co could lead to the observed features. These results support a process which can be described in its most simplified representation by equations (6)–(7).

$$CoTPPB_1B_2 \xrightarrow{h\nu} CoTPPB_1B_2^* \qquad (6a)$$

$$CoTPPB_1B_2^* \longrightarrow [CoTPPB_1\square] + B_2 \qquad (6b)$$

$$[CoTPPB_1\square] + O_2 \rightleftharpoons CoTPPB_1(O_2) \qquad (7)$$

Equation (6b) corresponds to the dissociation of one axially bound ether oxygen or water molecule (symbolized arbitrarily by B_1 or B_2), while equation (7) represents the complexation step of dioxygen to the vacant axial position of a short-lived cobalt porphyrin species. The analogy between equations (7) and (2) is only formal: there is a major difference with the spontaneous complexation described by (2) since here a photostationary state totally displaced to the right is obtained. This hypothesis is reinforced by results obtained under narrow bandwidth irradiation in the Soret band (8 nm) which lead to the same results but allowed the determination of quantum yields. The low quantum yield of the complexation (Table 2) reflects either the difference in concentration of the competing ligands (O_2, H_2O, ether group of Triton), corrected for their relative diffusion coefficients and for an orientation factor, or the existence of a tight solvent cage promoting geminate recombination, as the quantum yield of the ligand photodissociation itself is certainly high.[26b,c]

The dioxygen photodissociation was next shown to be operative on $Co^{II}TPP$ complexed to dioxygen when irradiation is carried out at 430 nm. It is, of course, in competition with the spontaneous ground-state process. Quantum yields corrected for the latter are even lower than those measured for complexation (Table 2). These results favour an interpretation of the low yields based on the presence of a tight solvent cage promoting an efficient geminate recombination. This feature should be ascribed to some specific interaction between the porphyrin and the micellar interface. This behaviour is very similar to that observed during the photodissociation of oxyhemoglobin[26b] but this does not imply that the interactions involved are identical.

This specific interaction should be sensitive to a reorientation of the porphyrin ring with respect to the interface. So all the experiments reported above were carried on $Co^{II}TPP$ and on two Co^{II}-*meso*-tetraphenylporphyrins substituted with one or four $(CH_2)_{15}CH_3$ chains, respectively (see earlier footnote). Absorption maxima and quantum yields for the dioxygen complexation following photodeligandation and for the photodissociation of dioxygen in these molecules are also shown in Tables 1 and 2. These photochemical studies were carried out using selective irradiation in the Soret band but the same behaviour has been observed using selective irradiation in the visible band. In the latter case, only qualitative results were obtained since the low absorption coefficients around 525 and 550 nm and the strong overlap between the bands corresponding to the complexed and uncomplexed species preclude precise measurements. In all these experiments, as well as in those run in sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB), the Soret bands are always narrow, with a width at half height close to 17 nm. This implies that aggregates which have a broadened Soret band are not present in these systems.[27] Furthermore, aggregates could not lead to total and reversible transformations observed here. $Co^{II}TPP$ and $Co^{II}TPP(1)$ do not show spontaneous complexation even if the temperature is raised to 50 °C, which is the upper limit for the stability of these micellar solutions. The same is true if an axial base like pyridine is bound to $Co^{II}TPP$ and $Co^{II}TPP(1)$. The behaviour of $Co^{II}TPP(4)$ is different since at 20 °C spontaneous complexation is observed and at equilibrium the amount of complexed molecule is 20%. This value is raised to 50% when

Table 3. Activation energies for the ground-state processes involving dioxygen in micellar Triton solution. These values are derived from an Arrhenius plot of kinetic runs measured between 20 and 45 °C at 5 °C intervals.

	Complexation/kJ mol^{-1}	Decomplexation/kJ mol^{-1}
$\mathrm{Co^{II}TPP}$	—	45.6
$\mathrm{Co^{II}TPPB}$	—	32.4
$\mathrm{Co^{II}TPP(1)}$	—	20.1
$\mathrm{Co^{II}TPP(1)B}$	—	39.5
$\mathrm{Co^{II}TPP(4)}$	72	19.4
$\mathrm{Co^{II}TPP(4)B}$	47	14.1

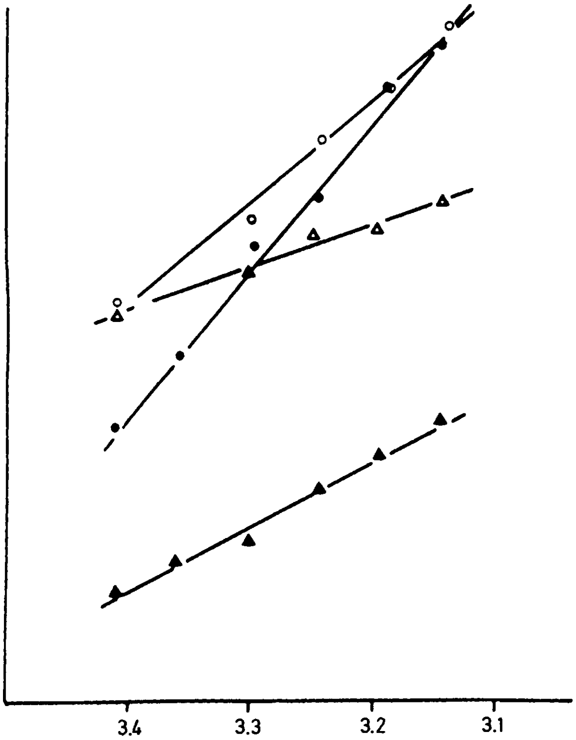


Figure 4. Arrhenius plots for the ground-state decomplexation of dioxygen in Triton X-100: ●, $\mathrm{Co^{II}TPP}$; ○, $\mathrm{Co^{II}TPPB}$; ▲, $\mathrm{Co^{II}TPP(4)}$; △, $\mathrm{Co^{II}TPP(4)B}$.

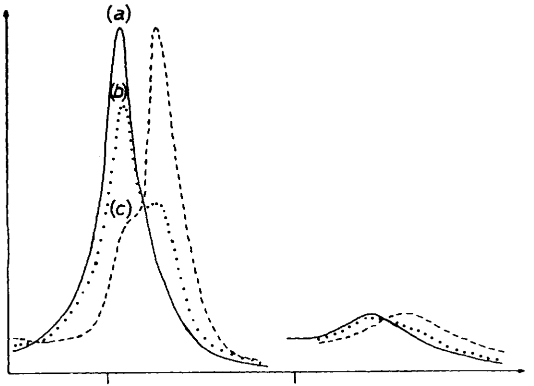


Figure 5. Evolution of the absorption spectrum of $\mathrm{Co^{II}TPP}$ in SDS micellar solutions: (*a*), freshly prepared degassed solution; (*b*), the same kept three days in the dark, in the presence of air; (*c*), previous solution irradiated 20 mn in the visible.

the sample is warmed to 40 °C. In the presence of the axial base,[12b] at 20 °C, the equilibrium concentration of $\mathrm{Co^{II}TPP(4)\text{-}BO_2}$ is 30%. Comparison between the two sets of molecules reveals an unexpected feature of such model dioxygen carriers. Orientation at the interface of the porphyrin, which depends on its hydrophilic–lipophilic balance (HLB), the latter being modified by the presence of an alkyl chain, is more important than the presence of a base in the axial position in the promotion of dioxygen complexation. The interplay of these parameters can also be seen in the values obtained for the activation energies of the thermal decomplexation of dioxygen (Table 3). These data are true activation energies when an equilibrium exists and can be considered as pseudo-activation energies in the case of $\mathrm{Co^{II}TPP}$ and $\mathrm{Co^{II}TPP(1)}$. In the latter case, the data are obtained as follows: visible irradiation is used to push the photostationary state towards the complexed state, the sample being at the required temperature. The kinetics of dissociation of dioxygen is then followed spectrophotometrically. The rate constants were measured for temperatures varying from 20 to 45 °C at 5 °C intervals. In this range an excellent linear correlation is obtained between the logarithms of the rate constants and the inverse temperatures (Figure 4).

The set of experiments cited above does not allow one to differentiate clearly between the role of the interface and that of the axial ligand in the initial step of the complexation of dioxygen triggered by photodeligandation. The interface provides polar solubilizing sites for these porphyrins, but a well chosen polar solvent could also provide such an environment,[21b] so that the specific effect of the interface would not appear in the photocomplexation step of dioxygen, but rather in the fact that this complexation is made reversible. The possible existence of a sixth ligand, *trans* to the photoejected ligand or to dioxygen entering the vacant site, must also be considered.[12b,15b] Also, there are many different ways to occupy both axial positions if water and the polyoxyethylenic chain are involved, and the latter may be complexed through one of the ether oxygen atoms, through the terminal oxygen atom of the hydroxy group or even through the phenoxy group at the other end of the Triton molecule. Statistical and steric considerations favour the first of these possibilities, even if the last one cannot be totally ruled out since it has been shown by Matsuo[28] that the affinity of the phenoxy groups for water could perturb micellar structures.

Ionic Detergent Solutions.—SDS micellar solutions. In the dark, an air saturated, freshly prepared solution of $\mathrm{Co^{II}TPP}$ in SDS appears to be a mixture containing 60 to 70% $\mathrm{Co^{II}TPPO_2}$. This apparently instantaneous complexation results from the fact that the porphyrin film deposited on the walls of the vial absorbs dioxygen. This affinity towards dioxygen has also been shown for monolayers of $\mathrm{Co^{II}TPP}$ on a quartz plate.[29c,d] If vacuum is applied over the sample the system totally reverts to the $\mathrm{Co^{II}TPP}$ species. When the latter solution is brought back in contact with the air, in the dark, a spontaneous but slow evolution leads in about twelve hours to the equilibrium mixture (Figure 5). Such a solution remains unchanged, in the absence of light, for about two to three weeks after which a broadening of the absorption bands is observed. Axial complexation of one pyridine, in the same conditions as for Triton solutions, induces no shift in the absorption maximum of the Soret band of the cobalt porphyrin, but in the presence of air, the kinetics of the ground-state complexation of dioxygen becomes faster and a complete shift to the complexed species is observed after 2 h for $\mathrm{Co^{II}TPP}$ and 15 min for $\mathrm{Co^{II}TPP(4)}$. As shown in Table 4, the wavelengths of the different bands are slightly shifted from their positions in Triton.

The determination of the activation energies for dioxygen binding and release were made in the same temperature range as for micellar Triton (Table 5). These activation energies are hardly depressed when the base is added to $\mathrm{Co^{II}TPP}$, but

Table 4. Wavelength of maximum absorbance at the Soret and visible bands in an aqueous micellar solution of SDS.

	Soret/nm		Visible/nm	
	I[a]	II[b]	I[a]	II[b]
Co$^{\mathrm{II}}$TTP	410	429	530	540
Co$^{\mathrm{II}}$TPPB	410	432	530	540
Co$^{\mathrm{II}}$TPP(4)	411	429	530	540
Co$^{\mathrm{II}}$TPP(4)B	411	432	530	540

B refers to pyridine bound in an axial position. [a] Porphyrin not complexed to dioxygen. [b] Porphyrin complexed to dioxygen.

Table 5. Activation energies for the ground-state processes involving dioxygen in micellar SDS solution. These values are derived from an Arrhenius plot of kinetic runs measured between 20 and 45 °C at 5 °C intervals.

	Complexation/kJ mol^{-1}	Decomplexation/kJ mol^{-1}
Co$^{\mathrm{II}}$TPP	17.8	68.7
Co$^{\mathrm{II}}$TPPB	12.7	60.0
Co$^{\mathrm{II}}$TPP(4)	—	24.8
Co$^{\mathrm{II}}$TPP(4)B	—	78.7

Table 6. $P_{\frac{1}{2}}O_2$ for various biological and artificial dioxygen carriers.

System	Solution	$P_{\frac{1}{2}}O_2$ (p/Torr)
Mb	Aqueous	0.70[a]
Hb	Aqueous	0.15–1.5[a]
FeTpivPP(MeIm)	Aqueous	38[b]
Co$^{\mathrm{II}}$TPP/SDS	Aqueous	1.1

[a] See ref. 5(*a*), (*d*). [b] See ref. 7.

Table 7. Quantum yields for the complexation of dioxygen triggered by photodeligandation and for its photodissociation in SDS solutions, at room temperature (values ±10%).

	Complexation ($10^3\varphi$)	Dissociation[a] ($10^3\varphi$)
Co$^{\mathrm{II}}$TPP	2.26	1.15
Co$^{\mathrm{II}}$TPPB	1.4	2.8
Co$^{\mathrm{II}}$TPP(4)	1.71	4.48
Co$^{\mathrm{II}}$TPP(4)B	1.87	2.36

[a] Solutions of the oxygenated complexes sealed under vacuum before irradiation.

addition of pyridine to Co$^{\mathrm{II}}$TPP(4) increased the activation energy by a factor of 3 for dioxygen release. A careful comparison of the results for both molecules show that it is the stability of Co$^{\mathrm{II}}$TPPO$_2$ which appears normal if results in Triton solutions are referred to. However this does not preclude the fact that the effect of the addition of the base leads to opposite results for these two detergents. This differing behaviour shows that the porphyrins are located close to the interface but interact with a different environment.

A study of the equilibrium of complexation as a function of the partial pressure of dioxygen, which was varied from 10 to 150 mmHg, leads to a $P_{\frac{1}{2}}O_2$ value of 1.1 mmHg at 20 °C, for Co$^{\mathrm{II}}$TPP. This parameter allows a direct comparison with published data (Table 6). Complexation of dioxygen following photodeligandation is also effective in these micellar solutions of SDS, as is the photodissociation (Table 7). In the latter experiments, values are corrected for the competitive ground-state decomplexation. Here also, addition of an axial base induces effects very different from those obtained in Triton (Table 7). The quantum yields of dioxygen complexation for Co$^{\mathrm{II}}$TPP and Co$^{\mathrm{II}}$TPP(4) decrease with addition of the base whereas they were increased by a factor of 15 and 2, respectively, in micellar Triton solutions. Hence the difference in the nature of the charge at the interface between Triton and SDS does not alone explain the observed phenomena. This is true even if the negative charges on the sulphonate groups polarize the π electrons of the porphyrin ring in SDS solutions. If we now turn our attention to the photodissociation, the presence of the axial base induces a marked but opposite effect on both compounds whereas the corresponding changes are negligible in Triton.

Table 8. Wavelength of maximum absorbance at the Soret and visible bands in aqueous micellar solution of CTAB.

	Soret/nm		Visible/nm	
	I[a]	II[b]	I[a]	II[b]
Co$^{\mathrm{II}}$TTP	411	430	530	540
Co$^{\mathrm{II}}$TPPB	411	432	530	540
Co$^{\mathrm{II}}$TPP(4)	411	430	530	540
Co$^{\mathrm{II}}$TPP(4)B	411	432	530	540

B refers to pyridine bound in an axial position. [a] Porphyrin not complexed to dioxygen. [b] Porphyrin complexed to dioxygen.

Table 9. Activation energies for the ground-state processes involving dioxygen in micellar CTAB solution. These values are derived from an Arrhenius plot of kinetic runs measured between 20 and 45 °C at 5 °C intervals.

	Complexation/kJ mol^{-1}	Decomplexation/kJ mol^{-1}
Co$^{\mathrm{II}}$TPP	54.9	36.8
Co$^{\mathrm{II}}$TPPB	28.5	52.6
Co$^{\mathrm{II}}$TPP(4)	48.7	17.7
Co$^{\mathrm{II}}$TPP(4)B	28.8	35.5

CTAB micellar solutions. In these ionic micelles, the polar heads are positively charged and comparison with the previous systems should bring some new information on these processes. Freshly prepared air saturated solutions form a 50/50 mixture of the free and dioxygen complexed metalloporphyrins, but these solutions do not show the stability observed for SDS and Triton. Degradation shows up after 72 h in the dark at room temperature. The Soret band becomes much wider on the short wavelength side and loses intensity. This is probably due to an association or an aggregation followed by an unknown oxidative process. Total reversibility of the complexation may nevertheless be obtained with freshly prepared solutions. The absorption maximum reverts from 430 to 411 nm (Table 8).

The activation energy parameters have also been determined for these systems and results are listed in Table 9. It can be seen that with the exception of Co$^{\mathrm{II}}$TPP, the results corresponding to complexation of pyridine are opposite to those obtained in SDS, so in the dark, activation energies for dioxygen complexation are higher than for decomplexation, the largest difference being observed for Co$^{\mathrm{II}}$TPP itself where they amount to 54.9 and 36.8 kJ mol^{-1} dm^3, respectively.

The complexation of dioxygen triggered by photodeligandation is also shown by these micellar solutions. To measure the quantum yields, the solutions are degassed and when all the porphyrin molecules have reached the uncomplexed state, air is introduced and mixed with the sample, after which exposure to light may begin. A photostationary state can be reached if

Table 10. Quantum yields for the complexation of dioxygen triggered by photodeligandation and for its photodissociation in CTAB solutions, at room temperature (values ±10%).

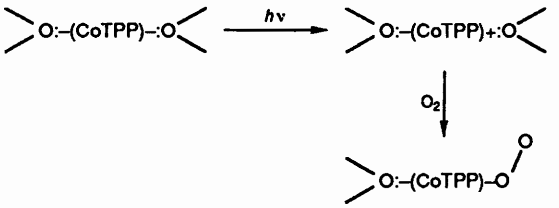
	Complexation ($10^3\varphi$)	Dissociation[a] ($10^3\varphi$)
$Co^{II}TPP$	2.73	1.61
$Co^{II}TPPB$	31.9	2.31
$Co^{II}TPP(4)$	9.13	8.20
$Co^{II}TPP(4)B$	6.82	3.43

[a] Solutions of the oxygenated complexes sealed under vacuum before irradiation.

irradiation lasts long enough. For $Co^{II}TPPB$ the equilibrium can be totally displaced towards the complexed form since the reverse process is very inefficient. All quantum yields values are corrected for these processes (Table 10). The efficiency of the photodissociation of dioxygen is smaller than that of the complexation triggered by photodeligandation and the largest contribution to the rate of the reaction is due to the spontaneous ground-state process, a situation which is very different from that observed for SDS solutions.

Discussion

We have shown here that in detergent solutions, whether they are non-ionic or ionic, cobalt porphyrins complex dioxygen following a photodeligandation. This constitutes a new reaction in the field of oxygen-transport model systems. The various ground state and photochemical experiments favour a mechanism in which the first step is the photodissociation of a bound water molecule or ether oxygen atom in the case of Triton. Dioxygen present in the solution then diffuses towards the free sixth co-ordination site on cobalt where it becomes co-ordinated (Scheme). The stability of the species so generated is very sensitive to the nature of the microenvironment and to the structure of the differently substituted porphyrins. From the experiments in Triton micellar solutions, we noted that orientation of the porphyrin at the interface, which depends on its HLB, is more important than the presence of a base in an axial position to promote a spontaneous dioxygen complexation. This unexpected result shows that solubilization at the interface is the crucial factor in the present observations.* The reverse trend is observed in ionic detergents. Analysis of the thermodynamic data shows that if one thinks of the activation energy as being a measure of the strength of the metal–dioxygen bond, $Co^{II}TPP$ and $Co^{II}TPP(4)$ behave in a similar way in Triton (Table 3). In these instances, the strength of the metal–dioxygen bond decreases when the axial base is present, whereas the contrary is true for $Co^{II}TPP(1)$. It should also be noted that activation energies relative to ground-state dioxygen release are not systematically smaller or larger than those relative to the complexation step. A change in the micellar medium (SDS, CTAB) may invert the relationships, even if some trends appear: on the whole, co-ordination of a base maximizes the activation energy for dioxygen release. These values compare well with those published[7e,14,15a,21] for carriers based on Co and Fe porphyrins. Where the necessary data to compute the entropy associated with dioxygen complexation is available, then values close to published data are obtainable, $S = -49.5$ eu for $Co^{II}TPP(1)$ and $S = -51.3$ eu for $Co^{II}TPP(4)$. Such highly negative values are linked to the loss of translational entropy of dioxygen upon binding. An added contribution may stem from a diminution of the rotational freedom due to geometric restriction affecting the bound dioxygen. Also, our results suggest that experiments carried out on dioxygen complexation to protohemes may have to be reassessed, since detergent concentration above the cmc was added to increase solubility, with the assumption that this addition had no effect.[30] A complete interpretation of these effects is presently unavailable, but the latter must be related to changes in the HLB and to the steric strains due to the presence of the alkyl substituents. Adding alkyl chains certainly does not prevent access of water or dioxygen to the cobalt atom. In Triton, the resulting steric crowding may, however, prevent an O-atom of the polyoxyethylene chain or the end OH group of the same chain from diffusing easily, after photodissociation, away from the cobalt atom and would promote its rapid recombination. This would fit with the much reduced measured quantum yields for dioxygen complexation observed when $Co^{II}TPP$ is alkylated with one or four chains in Triton (Table 2), and for the absence of such an effect in SDS or CTAB micellar solutions. A cage effect in the photodissociation must be operative if one considers the overall quantum yields which are always in the range 10^{-3} to 10^{-2}. The sensitivity of the thermodynamic parameters to the HLB of the porphyrin must be due to either a change in orientation at the micellar interface or to a change in the distance of the central Co atom to this interface. Now, the existence of the complexation triggered by a photodeligandation should not depend on the presence of the detergent as all that is needed is the presence of a photolabile ether-type oxygen ligand. The stability and reversibility of these model dioxygen carriers result from the properties of the interface: the intrinsic highly polar nature of the interface enhances the stability of the $Co–O_2$ bond[21b] which shows a partial $Co^{III}–O_2^{-\bullet}$ character, while micellar adsorption or solubilization provides, at the same time, the spatial segregation which is one of the factors at the origin of reversibility. The problem of the localization and orientation of the porphyrin is then very difficult to solve since the porphyrin must experience the polarizing effect of the interface and it must at the same time avoid protonation of the dioxygen ligand, which would initiate an irreversible process.[18a] Other explanations could certainly be given for the complexation step but it is felt that studies on a fast timescale are required for a deeper understanding.† The photodissociation of dioxygen from its adduct with $Co^{II}TPP$, which has also been shown above for Triton X-100 micellar solutions, has been confirmed recently by Hoshino,[31] who worked with methyltetrahydrofuran. Hoshino determined an approximate activation energy for decomplexation of 18.5 kJ mol^{-1} dm^3 which falls within the range of our data for Triton X-100 (Table 3). This result further substantiates our hypothesis of the involvement of Triton molecules *via* their



Scheme.

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* One may speculate, on the basis of these observations, about another possible role of the base in hemoglobin and in other natural carriers, as being that of a handle to fine tune the position of the porphyrin.

† For example, at the presentation of this work at the Atelier de Photochimie des Composés de Coordination in Paris, March 1985, it was suggested by Dr. D. G. Whitten that absorption of a photon by a loose complex (perhaps a CT) between CoTPP and O_2 might induce an electron transfer to dioxygen followed by the collapse of the $CoTPP^+ \cdots O_2^-$ ion pair to generate $CoTPP(O_2)$.

ether or phenyl groups. We also think that interactions of the phenyl rings of Triton with the phenyl rings of the tetraphenylporphyrin weaken the bonding interaction between cobalt and the Triton ether oxygen. This explanation fits with observations by Walker[32] and Wayland[33] who gave evidence of interaction between Co^{II} porphyrins and the molecules of toluene in which they were dissolved. The charge transfer interaction involves the π-donor character of the porphyrin and the π-acceptor character of toluene.[34]

Conclusion

In this work, we have shown the existence of a complexation of molecular oxygen following a photodeligandation of Co^{II} tetraphenyl porphyrins when they are solubilized in micellar solutions. This is a new reaction in the field of oxygen transport model systems. We have studied the efficiency of this reaction in different organized media and we conclude that there is a photodissociation of a ligand occupying an axial position of the cobalt atom, followed by a competitive recombination between oxygen and the ligand to the free site. We have determined a set of thermodynamic parameters concerning the $Co–O_2$ bond which shows that these systems are similar to model systems based on porphyrins modified by synthesis to protect one or both faces from interactions between carriers or between carriers and water molecules. The interesting feature of many of these systems lies in their room temperature reversibility in an essentially aqueous medium. It was the first model system[2a] to show this property and has been since observed for a heme in micellar Triton solutions.[35] Considering the values of the various thermodynamic parameters and of $P_{\frac{1}{2}}O_2$, these systems constitute a very good and simple model of biological dioxygen carriers.

We are presently working further on the specific role of ether groups in these processes.

Experimental

All solvents were of spectroscopic grade. Water was purified by ion-exchange on a mixed bed resin, then twice distilled over potassium permanganate and sulphuric acid. The 5,10,15,20-tetra-(2-hydroxyphenyl)porphyrin *O*-alkylated by four $(CH_2)_{15}CH_3$ chains and the 5-(2-hydroxyphenyl)-10,15,20-(triphenyl)-porphyrin *O*-alkylated by one hexadecyl chain were synthesized following a procedure given by Little,[29] and purified by silica-gel thin layer chromatography, after which they were metallized by Rothenmund's method[36] (the porphyrin with four alkyl substituents is a mixture of four atropoisomers of relative abundance *ca.* 1:4:2:1[37]).

5-(2-O-*Hexadecylphenyl*)-10,15,20-*triphenylporphyrin*.—5-(2 Hydroxyphenyl)porphyrin (48 mg) and 1-bromohexadecane (200 mg) were dissolved in DMF (10 cm^3) containing anhydrous potassium carbonate (200 mg) and stirred for two days at room temperature. The solution was concentrated, and the residue extracted with dichloromethane and washed with water. The organic layer was evaporated and the residue chromatographed on thin-layer silica gel (yield 92%). (Satisfactory microanalysis was obtained for $C_{60}H_{62}N_4O_4$, H_2O); $\lambda_{max}(CHCl_3)$ 421 (ε_{max} 311 000 $dm^3 mol^{-1} cm^{-1}$), 516 (12 000), 555, and 595 nm; $\delta_H(CDCl_3)$ 1.30 (31 H, m, $[CH_2]_{14}CH_3$), 2.78 (2 H, s, 2 × NH), 4.20 (2 H, t, OCH_2), 7.20 (2 H, s, 3-H, 5-H, 2 × Ar of *O*-hexadecylphenyl), 7.22 (4 H, t, 4-H, 4 × Ar), 7.55 (6 H, d, 3-H, 5-H, 3 × Ar), 8.08 (7 H, d, 2-H, 3 × Ar, 6-H, 4 × Ar), and 8.86 (8 H, s, H_β, pyrrole.)

5,10,15,20-*Tetra*-(2-O-*hexadecylphenyl*)*porphyrin*.—5,10,15,20-Tetra-(2 hydroxyphenyl)porphyrin (50 mg) and 1-bromohexadecane (1.3 g) were dissolved in DMF (15 cm^3) containing anhydrous potassium carbonate (200 mg) and stirred for two days at room temperature. The solution was concentrated, extracted with dichloromethane and washed with water. The organic layer was evaporated to dryness and the residue chromatographed on thin-layer silica gel (yield 64%). (Satisfactory microanalysis is obtained for $C_{108}H_{158}N_4O_4$, H_2O); $\lambda_{max}(CHCl_3)$ 421 (ε_{max} 420 300 $dm^3 mol^{-1} cm^{-1}$), 516 (18 000), 548 (6 200), 591 (6 100), and 646 nm (2 500); $\delta_H(CDCl_3)$, 0.65, 0.80, 0.90, 1.10, 1.27 (124 H, m, $[CH_2]_{15}CH_3$, four atropoisomers), 3.86 (8 H, t, OCH_2), 7.30 (8 H, m, 3-H, 5-H, 2 × Ar), 7.63, 7.75, 7.94, 8.02 (8 H, m, 4-H, 6-H, 4 × Ar), and 8.74 (8 H, s, H_β, pyrrole.)

Triton X-100 (Rohm & Hass) was carefully checked for peroxides.[38] In the first runs comparisons were made with samples purified chromatographically over silica gel,[39] but this did not affect the overall behaviour. It was observed experimentally that removal of peroxides was very important. Sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB) (both from Merck) were recrystallized twice from ethanol 95% and triply distilled water, respectively.

Preparation and Handling of Samples.—All operations were carried out in a dark room equipped with red safe lights. To prepare a sample, a fresh hexane solution of the selected porphyrin, CoTPP, CoTPP(1) or CoTPP(4) of known absorbancy (between 0.5 and 1.5 for a 10 mm path) was poured into a 25 cm^3 vial. The solution was evaporated under light vacuum at room temperature as the tilted vial rotated. The thin film of porphyrin deposited on the wall and the bottom of the vial was pumped at 10^{-4} Torr* to remove any solvent left and a known volume of the detergent solution (Triton, 5×10^{-3} mol dm^{-3}; SDS, 30×10^{-3} mol dm^{-3} and CTAB 5×10^{-3} mol dm^{-3}) was added to give an absorbance at the Soret band of about one unit for a 1 cm path cell. The sample was sonicated for 30 s and then generally left in the dark at 36 °C for 36 to 48 h, during which time it was hand-shaken twice a day for a few seconds. Before use the solution was filtered over a 0.22 μ GSWP Millipore filter. Electronic spectra were recorded with a Varian Superscan III or a Pye-Unicam SP8-400 spectrophotometer equipped with thermostatted cell holders. Rates were calculated from the first-order plot of three or more half-lives.

Qualitative irradiations were carried out in the sunlight, or with a solar simulator built around a compact 250 W tungsten–iodine lamp set at the focus of a parabolic dichroic mirror and fitted with a 10 cm running water filter. Cut-off (CS 0-51, 3-73, 3-68) and band-pass (C5 4-96) Corning-glass filters were added when required. Due to the close proximity of the Soret bands of the uncomplexed and complexed porphyrins, liquid solution filters were sometimes added in a 1 cm cell. They consisted of solutions of CoTPP in various solvents chosen such that their Soret bands matched that which had to be protected, namely in the region 410 and 430 nm. For the latter wavelength, the filter solution must be pre-irradiated in the visible as described in the Results section.

Quantum-yield measurements were performed on an optical bench carrying a Bausch and Lomb high-intensity grating monochromator fitted with a 150 W XBO lamp. Potassium ferrioxalate was used as an actinometer.[40] Alternatively, light intensity was measured with a Photodyne XLA-88 radiometer. In kinetic runs, transmitted light was detected with a 1P28 photomultiplier using narrow slits on a Jobin-Yvon H20 monochromator. Light reflected off the irradiation beam gave a reference for ratio recording. ESR spectra were run on a Brüker ER420 spectrometer fitted with an ER400X-RL or TR4102 cavity, a B-ST 100/700 variable temperature controller and a

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* 1 Torr = 133.322 Pa.

Nicolet 535 accumulator. Cylindrical 4 mm quartz tubes or flat 1 mm cells were used. Photolysis in the cavity was performed with a 1000 W xenon lamp using a MTO A408 C' filter.

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