141. The Vitamin-B_{12}-derived Co(III)-Complex 'Pyrocobester' as Photosensitizer and as Substrate in Reactions Involving 'Singlet Oxygen'

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Summary

The vitamin-B_{12} derivative 'pyrocobester' (**1**) acts as photosensitizer in its light-induced oxygenation which involves 'singlet oxygen' ($^1O_2$) and which gives '5,6-dioxosecopyrocobester' (**2**) cleanly. The identity of the photosensitizer is deduced from a match of the 'photochemical action spectrum' of the photooxygenation with the UV/VIS absorption spectrum of **1**. The involvement of $^1O_2$ in this reaction is established on the basis of solvent and solvent H/D isotope effects, of quenching studies with β-carotene and of competition experiments with 9,10-dimethylanthracene. Also, decomposition of the thermal $^1O_2$-source 1,4-dimethylnaphthalene-1,4-endoperoxide in a solution of **1** induces a clean oxygenation of **1** to **2** in the dark as well.

To date, information on physical and chemical properties of electronically excited Co(III)-corrins still is linked (largely) to the chemical results of the light-induced cleavage of an axial ligand-metal bond in such (and related) Co(III)-compounds [1]. In particular also, the search for (photoinduced) luminescence from corrinoid Co(III)-complexes has remained without success [2], in contrast to the characteristic luminescence of their metal-free ligands [3]. Apparently, the chelated (diamagnetic) transition metal ion Co(III) mediates rapid (radiationless) deactivation of (the) ligand-centered electronically excited states of Co(III)-corrins[2]).

Recently, we observed the vitamin-B_{12}-derived Co(III)-B-didehydrocorrin 'pyrocobester' (**1**, hexamethyl *Coa, Coβ*-dicyano-7-de(carboxymethyl)-7,8-didehydrocobyrinate [6]) to undergo an efficient photooxygenation reaction giving '5,6-dioxosecopyrocobester' (**2**, hexamethyl *Coa, Coβ*-dicyano-5,6-dioxo-7-de(carboxymethyl)-7,8-didehydro-5,6-secocobyrinate) cleanly [7] *(Scheme 1)*. The constitution of **2** and the chemical stability of **1** in solution in the absence of light or of molecular oxygen indicated a photooxygenation of **1**, possibly with participation of 'singlet oxygen' ($^1O_2$) [8]. Accordingly, this finding offered a potential opportunity to

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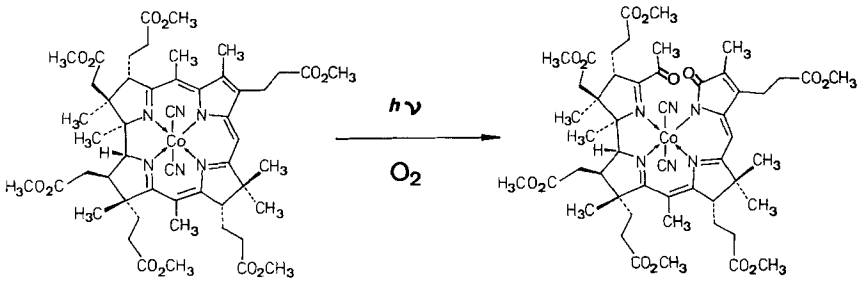
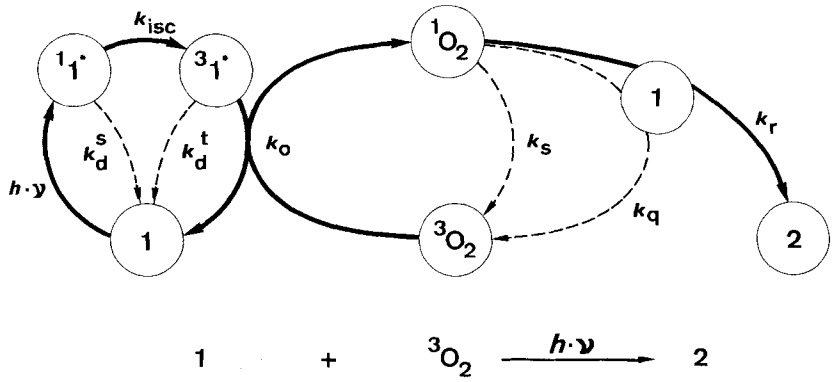
uncover a new aspect of the excited-state chemistry of Co(III)-corrins (in the form of an energy transfer to molecular oxygen)[2]), as well as to explore the previously unknown reactivity of Co(III)-corrins towards $^1O_2$[3]). For this purpose it remained to clarify in detail the suggested, unexpected role of the Co(III)-complex **1** as a photosensitizer and the involvement of $^1O_2$ in the photooxygenation of **1**.



1 **2**

To characterize the (hypothetical) intermediate stages in the photooxygenation of **1** (to give **2**), a conventional reaction sequence for a self-sensitized photooxygenation [8b] [11] [12] is used as a working hypothesis to be tested in a kinetic analysis *(Scheme 2)*:



[2]) The investigations [2] of the luminescence properties of various metal complexes of the synthetic corrin ligand 1,2,2,7,7,12,12-heptamethylcorrin-15-carbonitrile [4a] (which stood in context with the photoinduced A/D-secocorrin → corrin cycloisomerization [4b] [4c]) allowed to correlate (also) the effect of the coordinated metal ion on the luminescence of the metallocorrin with the ability of the metallocorrin to sensitize photooxygenation reactions involving 'singlet oxygen' [5]. In this respect the dicyanocobalt(III) 1,2,2,7,7,12,12-heptamethyl-15-cyanocorrinate was found to show hardly any activity as photosensitizer in reactions of $^1O_2$ [5].

[3]) In the meantime photooxygenation has been applied also to the parent Co(III)-corrin 'cobester' (**3**, heptamethyl *Coa, Coβ*-dicyanocobyrinate [9]) and promises to be useful for the purpose of preparing secocorrinoid Co(III)-complexes derived from vitamin B_{12} [10].

Photoexcited **1** (^{1}**1***; *Eqn. 1*) intersystem crosses to its triplet excited state (^{3}**1***; *Eqn. 2*) before[4]) transfer of electronic excitation energy onto $^3O_2$ occurs, to give molecular oxygen in its excited singlet state ('singlet oxygen', $^1O_2$ ($^1\Delta_g$), *Eqn. 3*). $^1O_2$ then reacts with (a second ground-state molecule[5]) of) **1** to give **2** *(Eqn. 4)*, in competition with its possible 'physical' deactivation by **1** *(Eqn. 5)*, by the solvent S *(Eqn. 6)* or by an added quencher Q *(Eqn. 7)* as well as with its chemical removal by the '$^1O_2$-trap' A *(Eqn. 8)* [11] [12].

$$\mathbf{1} + h\nu \rightarrow {}^1\mathbf{1}^* \tag{1}$$

$$^1\mathbf{1}^* \xrightarrow{(k_{isc})} {}^3\mathbf{1}^* \tag{2}$$

$$^3\mathbf{1}^* + {}^3O_2 \xrightarrow{(k_o)} \mathbf{1} + {}^1O_2 \tag{3}$$

$$\mathbf{1} + {}^1O_2 \xrightarrow{(k_r)} \mathbf{2} \tag{4}$$

$$\mathbf{1} + {}^1O_2 \xrightarrow{(k_q)} \mathbf{1} + {}^3O_2 \tag{5}$$

$$S + {}^1O_2 \xrightarrow{(k_s)} S + {}^3O_2 \tag{6}$$

$$Q + {}^1O_2 \xrightarrow{(k_q^Q)} Q + {}^3O_2 \tag{7}$$

$$A + {}^1O_2 \xrightarrow{(k_A)} AO_2 \tag{8}$$

On the Nature of the Photosensitizer. For an experiment with continuous irradiation, the rate of disappearance of **1** ($-dN_1/dt$), determined from analysis of the absorption spectra of the solutions (see *Fig. 1*), can be converted to a characteristic of the chemical system investigated, the photochemical quantum yield of disappearance of **1** (Φ_{-1}) [15] [16]:

$$-\frac{dN_1}{dt} = \Phi_{-1}^{\lambda} \cdot I_0^{\lambda} (1 - 10^{-\varepsilon_1^{\lambda} \cdot c_1 \cdot l}) \tag{9}$$

Eqn. 9[6]) predicts a characteristic dependence of the kinetics of the photooxygenation of **1** on the light absorption by **1**, expressed by the contribution OD_1^{λ} of **1** to the optical density (OD^{λ}) of the sample solution at the wavelength λ. Analysis is simplified, when

$$OD_1^{\lambda} \approx OD^{\lambda}, \tag{10}$$

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[4]) This simplifying assumption is made in analogy to the situation with organic molecules, which in general photosensitize reactions with $^1O_2$ more effectively from their triplet electronically excited states [13] (but is without direct consequences for the problems addressed here).

[5]) It is conceivable that $^1O_2$ reacts with the sensitizer in the original solvent cage [14], but this is highly improbable (here) in view of the estimated rates of reactions between **1** and $^1O_2$.

[6]) Abbreviations used: I_0^{λ} = intensity of irradiation on sample cell as function of irradiating wavelength (photons/s); ε_1^{λ} = molar extinction coefficient of **1** (l/mol · cm); c_1, c_{O_2}, c_Q and c_A = concentration

i.e. for sufficiently small photochemical conversion and, independently of the progress of the reaction, for irradiations in the long-wavelength part of the spectrum, at $\lambda \geq 700$ nm (see *Fig. 1*). (For this reason, when possible for the photochemical experiments in this investigation, illuminations were performed at $\lambda = 710$ nm.)

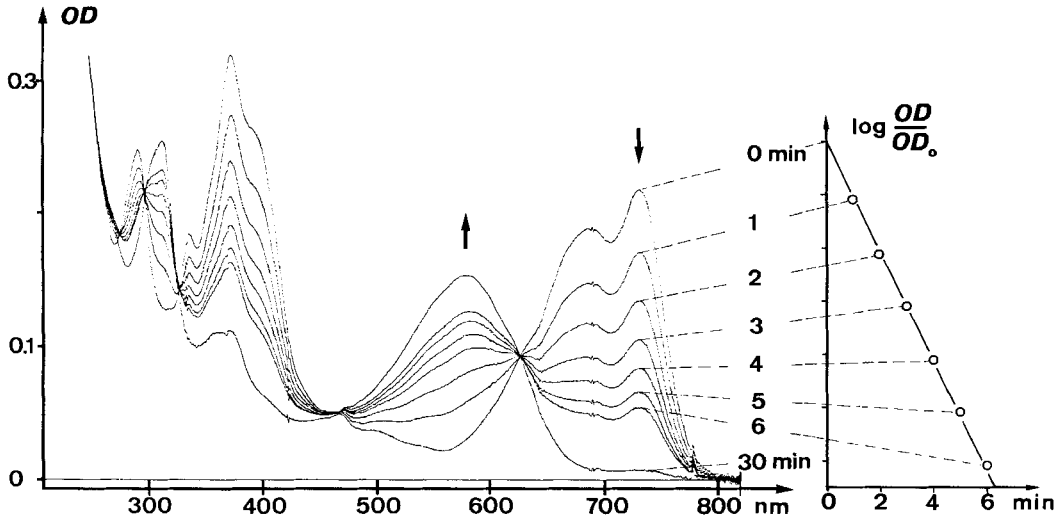

Fig. 1. *Changes in the UV/VIS-Absorption Spectrum* (left) *and Kinetic Analysis of the Decrease of the Optical Density at 730 nm* (right) *during the Photooxygenation of 'Pyrocobester'* (**1**) *in* CCl_4. Wavelength of exciting light: 710 nm; initial concentration of **1**: $1.56 \cdot 10^{-4}$ mol/l; O_2 (1 atm); $20 \pm 2°$; 0.1-cm path length.

Under these conditions, since

$$OD^{\lambda} \approx OD_1^{\lambda} = \varepsilon_1^{\lambda} \cdot c_1 \cdot l \tag{11}$$

and with sufficiently small OD^{λ} *Eqn. 9*[6]) reduces [15] [16a] to

$$-\frac{dN_1}{dt} \cong I_0^{\lambda} \cdot \Phi_{-1}^{\lambda} \cdot 2.303 \cdot OD^{\lambda} \tag{12}$$

In such a situation, and under the condition that Φ_{-1} is wavelength-independent in the range investigated, the wavelength dependence of the experimental rate of

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of **1**, $^3O_2$, Q, and A, respectively (mol/l); k_{isc} = rate of intersystem crossing $^1\mathbf{1}^* \rightarrow {}^3\mathbf{1}^*$ (s^{-1}); k_d^s (k_d^t) = rate of deactivation of $^1\mathbf{1}^*$ ($^3\mathbf{1}^*$) by processes other than intersystem crossing (other than quenching by $^3O_2$) (s^{-1}); k_0 = rate constant for quenching of $^3\mathbf{1}^*$ by $^3O_2$ to give $^1O_2$ (l/mol · s); k_r (k_q) = rate constant for chemical reaction (deactivation) of $^1O_2$ with **1** to give **2** (or $^3O_2 + \mathbf{1}$) (l/mol · s); k_s = rate of deactivation of $^1O_2$ by solvent (s^{-1}); k_q^Q = rate constant for deactivation of $^1O_2$ by Q (l/mol · s); k_A = rate constant for reaction of A with $^1O_2$ (l/mol · s); index^H and index^D refer to undeuterated and deuterated solvent, respectively.

disappearance of **1** (the 'photochemical action spectrum' [17]) should parallel the OD^{λ} of the solution and correspondingly the absorption spectrum of **1**, if it were the photosensitizing species.

Monochromatic irradiation of oxygen-saturated solutions of **1** in CCl_4 ($c_1 = 1.56 \cdot 10^{-4}$ mol/l) at regularly spaced wavelengths between 800 and 350 nm led to disappearance of **1** and formation of **2** in a clean reaction (exhibiting isosbestic points)[7]). For the irradiation at 710 nm it was established, that (under the specific conditions) the rate of reaction depends on c_1 in first-order (see *Fig. 1*). A plot of the experimentally derived rates of disappearance of **1** *vs.* wavelength λ (for a reaction exhibiting pseudo-first-order kinetics with respect to c_1 and corrected for the wavelength dependence of I_0^{λ}) resulted in the 'photochemical action spectrum', as shown in *Fig. 2* (see also *Exper. Part*).

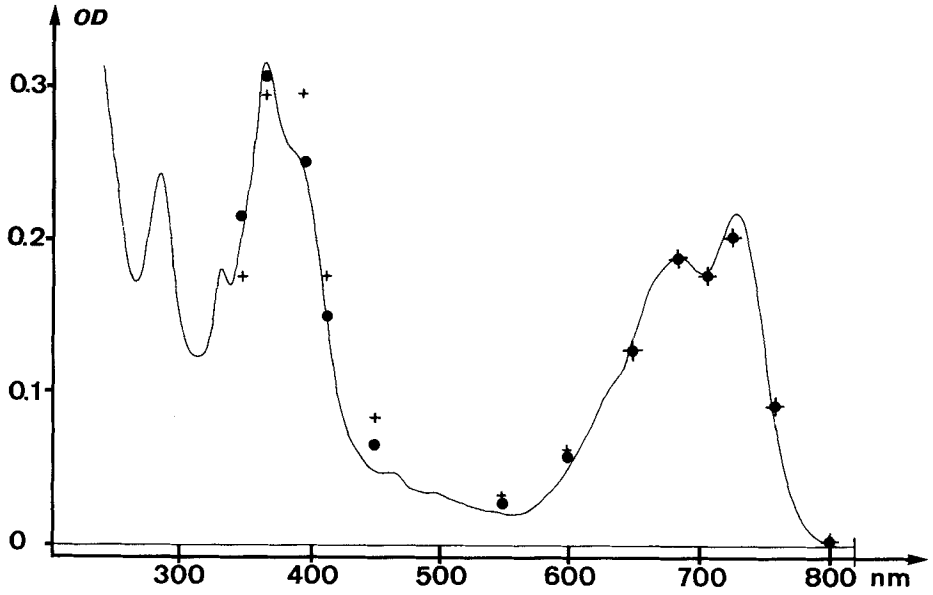

Fig. 2. *Comparison of the UV/VIS-Absorption Spectrum of* **1** *with the 'Photochemical Action Spectrum' for the Photooxygenation of* **1** *in* CCl_4 (calibration point at 690 nm): (+) = actual relative rate of photooxygenation of **1** due to irradiation at the specified wavelength; (●) = relative rate of photooxygenation of **1** corrected for the wavelength dependence of light intensity (exper. conditions as in *Fig. 1*).

By comparison with the UV/VIS-absorption spectrum of **1**, it is evident that light absorption by **1** and rate of photooxygenation of **1** exhibit a closely related wavelength dependence, allowing to assign to **1** the role of the photosensitizer in the photooxygenation **1** → **2**. Furthermore, a pronounced dependence of Φ_{-1} on λ (in the range of 350 to 800 nm) is not indicated by these experiments[7]).

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[7]) The conversion **1** → **2** was also checked by TLC (see *Exper. Part*). Irradiation at $\lambda < 350$ nm (*e.g.* at 310 nm) leads to formation of several (unidentified) side products as major reaction paths.

On the Role of 'Singlet Oxygen' in the Photooxygenation of **1**. To test for the intermediate involvement of 'singlet oxygen' ($^1O_2$) indirectly[8]), the kinetic characteristics of the oxygenation reaction are correlated with the known properties of $^1O_2$ [8c–g] [20]. Of the criteria at hand, specifically the (inherent) lifetime of $^1O_2$ in solution has been examined in detail [11] [15] [21]: it can be steered in characteristic fashion by the chemical [21] and H/D-isotopic [21] [22] composition of the solvent, by the concentration of an added $^1O_2$-quencher Q (*e.g.* β-carotene [11] [23]) or of a characterized '$^1O_2$-trap' (*e.g.* diphenylisobenzofurane (DPBF) [24] or 9,10-dimethylanthracene (9,10-DMA) [12a] [25]), but (in general) also depends upon the concentration of the $^1O_2$-sensitizer and/or -substrate in the solution [11a] [26].

With respect to the photooxygenation reaction **1** → **2**, presented in *Scheme 1*, Φ_{-1} of *Eqn. 9* can be expressed in terms of the quantum yield of photogeneration of $^1O_2$ by **1** ($\Phi_{^1O_2}$) and the state efficiency of photooxygenation of **1** by $^1O_2$ (ϕ_{-1}) (applying the 'steady-state approximation' [27]) [11][6]):

$$\Phi_{-1} = \Phi_{^1O_2} \cdot \phi_{-1} \tag{13}$$

$$\Phi_{^1O_2} = \frac{k_{isc}}{k_d^s + k_{isc}} \cdot \frac{k_0 \cdot c_{O_2}}{k_d^t + k_0 \cdot c_{O_2}} \tag{14}$$

$$\phi_{-1} = \frac{k_r \cdot c_1}{(k_r + k_q) c_1 + k_s + k_q^Q \cdot c_Q + k_A \cdot c_A} \tag{15}$$

Specifically, in the absence of the $^1O_2$-quencher Q and the chemical '$^1O_2$-trap' A, *Eqn. 13* and *15* reduce to

$$\Phi_{-1} = \Phi_{^1O_2} \cdot \frac{k_r \cdot c_1}{(k_r + k_q) c_1 + k_s} \tag{16}$$

For a convenient analysis, *Eqn. 16* is commonly [11] [28] expressed in reciprocal form

$$(\Phi_{-1})^{-1} = (\Phi_{^1O_2})^{-1} \cdot \left[1 + \frac{k_q}{k_r} + \frac{k_s}{k_r} \cdot (c_1)^{-1}\right] \tag{17}$$

signifying a linear dependence of $(\Phi_{-1})^{-1}$ on $(c_1)^{-1}$ [11] [28]. The slope of such a plot (*i.e.* $(\Phi_{^1O_2})^{-1} \cdot k_s/k_r$) is proportional to the rate of deactivation of $^1O_2$ by the solvent, k_s (or inversely proportional to the inherent lifetime of $^1O_2$ in the solvent, $\tau_s = 1/k_s$).

Since $^1O_2$ is deactivated much slower by a deuterated than by the corresponding undeuterated solvent (*i.e.* $k_s^H \gg k_s^{D}$[6]), as has been determined for a large variety of organic solvents [21] [22]), the slopes of such plots should differ considerably for two comparable experiments, one in the deuterated and the other in the undeuterated solvent. In fact, under the conditions that $\Phi_{^1O_2}$ as well as k_q and k_r do

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[8]) $^1O_2$ can also be detected directly due to its luminescence at 1270 nm [18] as well as the 'dimole'-emission at 634/704 nm [19].

not depend significantly on the H/D-isotopic composition of the solvent, the ratio of the slopes from such plots (as based on *Eqn. 17*) yields a solvent H/D-isotope effect that can be identified with k_s^H/k_s^D. Furthermore, a common intercept of such plots (at $(c_1)^{-1}=0$) signifies insensitivity of $\Phi_{^1O_2}$ to the H/D content of the solvent (*i.e.* $\Phi^H_{^1O_2} \approx \Phi^D_{^1O_2}$)[6]). Since k_s^H typically exceeds k_s^D by a factor of 10 or more [21] [22], solvent H/D isotope effects on photooxygenation reactions are an excellent criterium for the intermediacy of $^1O_2$ (see below).

Solvent H/D Isotope Effects on the Photooxygenation of **1**. A strong enhancement of the rate of photooxygenation of **1** was observed, when $CDCl_3$ or C_6D_6 were chosen as solvents, instead of $CHCl_3$ or C_6H_6. Also in the sequence CH_3OH, CH_3OD and CD_3OD comparable solvent H/D isotope effects were found for replacement (D for H) of both types of H-atoms (hydroxy or methyl). In this way, CD_3OD outmatched even the '$^1O_2$-super solvent' CCl_4 [22] with respect to the efficiency of photooxygenation of **1** at sufficiently high concentrations of **1**. The three sets of experiments (see the *Table*) were analyzed in terms of *Eqn. 17*, resulting in the plots shown in *Fig. 3–5*. *Fig. 3* represents a graphical analysis of the photooxygenation of **1** in CH_3OH, CH_3OD and CD_3OD. Characteristically, the slopes of the plots with the relative values 31:12:1 stand for a correspondingly large solvent H/D isotope effect on the lifetime of $^1O_2$ in these solvents. In contrast, an intercept (at $(c_1)^{-1}=0$) nearly common for the three H/D-isotopically labelled forms of methanol, signifies absence of a noticeable solvent H/D isotope effect on $\Phi_{^1O_2}$ (s. *Eqn. 17*).

Similar plots were obtained for the analysis of the photooxygenation of **1** in $CHCl_3$ and $CDCl_3$ *(Fig. 4)* and for C_6H_6 and C_6D_6 *(Fig. 5)*. For these experiments also, a common intercept characterizes $\Phi_{^1O_2}$ in the deuterated and in the undeuterated solvent systems, while the strongly larger slope for the undeuterated solvent

Table. *Influence of the Solvent and Solvent H/D Isotope Effects on the Rate of Photooxygenation of* **1** (at 20±2°; O_2 (1 atm); λ = 710 nm)

Solvent	c_1[a])	$\rho_{D,H}$[b])	c_1[a])	k_{rel}[c])	$\rho_{D,H}$[b])	k_s^H/k_s^D[d])
CH_3OH	1.4		0.14	1		
CH_3OD	1.4	2.1	0.14	2.4	2.4	2.6
CD_3OD	1.4	11.7	0.14	26	26	31
$CHCl_3$	1.6		0.16	1.4		
$CDCl_3$	1.5	3.5	0.15	13	9.2	17
C_6H_6	1.3		0.13	0.4		
C_6D_6	1.3	4.7	0.13	4.2	10.4	15
CCl_4	–	–	0.15	14	–	–

[a]) Initial concentration of **1** (mmol/l).

[b]) Apparent solvent H/D isotope effect on the rate of photooxygenation of **1**, calculated with *Eqn. 18*.

[c]) Approximate, initial relative rate of disappearance of **1**, calibrated with respect to the experiment in CH_3OH.

[d]) Ratio of rates of deactivation of $^1O_2$ in the undeuterated (k_s^H) *vs.* in the deuterated solvent (k_s^D), calculated with *Eqn. 17*.

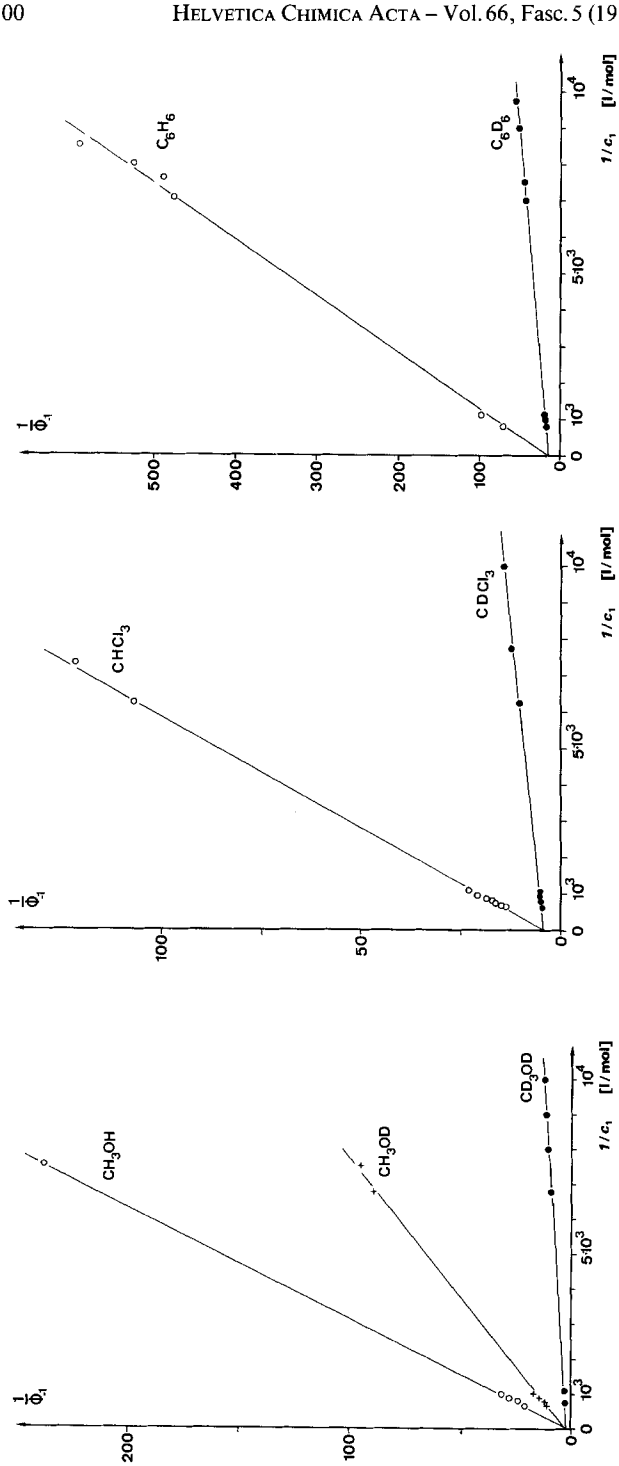

Fig. 3. *Analysis of the Rate of Photooxygenation of* **1** *in CH_3OH, CH_3OD and in CD_3OD by 'Double-reciprocal Plots'* [11] (see *Eqn. 17*). Wavelength of exciting light: 710 nm; O_2 (1 atm); $20 \pm 2°$; path lengths: 1 cm for $c_1 < 2 \cdot 10^{-4}$ mol/l and 0.1 cm for $c_1 \gtrsim 10^{-3}$ mol/l. ϕ_{-1}, the state efficiency of photooxygenation (see *Eqn. 13*), is estimated *via* the rate of generation of $^1O_2$, determined indirectly by the rate of photooxygenation of 9,10-DMA in CD_3OD and photosensitized by **1** (see below).

Fig. 4. *Analysis of the Photooxygenation of* **1** *in $CHCl_3$ and in $CDCl_3$ by 'Double-reciprocal Plots'* (see *Eqn. 17*). Exper. conditions as in *Fig. 3*, but using the rate of photooxygenation of 9,10-DMA in $CHCl_3$ and $CDCl_3$ to estimate the rate of generation of $^1O_2$ photosensitized by **1**.

Fig. 5. *Analysis of the Photooxygenation of* **1** *in C_6H_6 and in C_6D_6 by 'Double-reciprocal Plots'* (see *Eqn. 17*). Exper. conditions as in *Fig. 3*, but using the rate of photooxygenation of 9,10-DMA in C_6H_6 and in C_6D_6 to estimate the rate of generation of $^1O_2$ photosensitized by **1**.

in both cases corresponds to the expected ratio (k_s^H/k_s^D) from more recently published values for the solvent H/D isotope effect on the lifetime of $^1O_2$ in solution [22][9]).

With these results, a quantitative correlation between the observed effect of the solvent H/D isotopic composition on the photooxygenation of **1** and theoretically expected effect on a reaction involving $^1O_2$ is apparent.

However, notice that $\rho_{D,H}$, the observed solvent H/D isotope effect on the rate of photooxygenation, taken from conventional kinetic analysis, and defined as in *Eqn. 18* and *19*[6])

$$\rho_{D,H} = \Phi_{-1}^D/\Phi_{-1}^H \tag{18}$$

$$\rho_{D,H} = \frac{\Phi_{^1O_2}^D \cdot k_r^D [(k_r^H + k_q^H)c_1 + k_s^H]}{\Phi_{^1O_2}^H \cdot k_r^H [(k_r^D + k_q^D)c_1 + k_s^D]}, \tag{19}$$

in general, is considerably smaller than k_s^H/k_s^D, a fact that actually is obscured by the double-reciprocal plots of the type $(\phi_{-1})^{-1}$ *vs.* $(c_1)^{-1}$.

Specifically, $\rho_{D,H}$ depends upon c_1[10]), and with

$$\beta^H = k_s^H \cdot \frac{1}{(k_r^H + k_q^H)} \tag{20}$$

and

$$\beta^D = k_s^D \cdot \frac{1}{(k_r^D + k_q^D)} \tag{21}$$

$\rho_{D,H}$ decreases towards 1.0[11]) for $c_1 \gg \beta^H$ (independently of k_s^H/k_s^D) in a reaction involving $^1O_2$, while it approaches k_s^H/k_s^D only for $c_1 \ll \beta^D$.

To illustrate this point quantitatively, the actual $\rho_{D,H}$, as obtained from the rate data, is also included in the *Table*. As a consequence, the observation of a solvent H/D isotope effect $\rho_{D,H}$ considerably smaller than k_s^H/k_s^D (in general) should not be used as a criterium to exclude the involvement of $^1O_2$ in a (photo)oxygenation reaction, without information on its concentration dependence[12]).

Effects of the Concentration of **1**. It is apparent from above that c_1 plays a crucial role in the kinetics of the photooxygenation of **1**, (specifically) due to its effect on ϕ_{-1}, the state efficiency of reaction of **1** with $^1O_2$ to give **2**. Qualitatively,

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[9]) From our results in CD_3OD as solvent, $\tau_{CD_3OD} \approx 300$ μs can be estimated, based on $\tau_{CH_3OH} \approx 10$ μs [22b] [23b] [29].

[10]) Recently, attention was drawn to such pitfalls of 'one point' experiments [11a] [26a] involving solvent H/D isotope effects in photooxygenation reactions, and a dependence of $\rho_{D,H}$ on the concentration of the sensitizer [26b] as well as the substrate [10] were demonstrated in a qualitative way.

[11]) Assuming $\Phi_{^1O_2}^H \approx \Phi_{^1O_2}^D$, $k_r^H \approx k_r^D$ and $k_q^H \approx k_q^D$.

[12]) This point might be important especially for the interpretation of information from preparative results (e.g. [10]).

this effect of c_1 can be characterized by consideration of the two limiting cases applied to *Eqn. 16:*

$$\phi_{-1} \approx \frac{k_r \cdot c_1}{k_s} \text{ for } c_1 \ll \beta \text{ (case I)}^{13}) \tag{22}$$

and

$$\phi_{-1} \approx \frac{k_r}{k_r + k_q} \text{ for } c_1 \gg \beta \text{ (case II)}^{14}) \tag{23}$$

Correspondingly, when $OD^{710} > 1.5$ (*i.e.*, the light absorption is practically independent of changes of c_1), the photooxygenation of **1** is found to follow a rate law that depends upon c_1 in first-order at low c_1 (case I; *e.g.* for $c_1 \leqslant 1.5 \cdot 10^{-4}$ mol/l in the undeuterated solvents of the *Table* and in CH_3OD), while at $c_1 \geqslant 1.3 \cdot 10^{-3}$ mol/l the photooxygenation of **1** proceeds at a nearly c_1-independent rate in the perdeuterated solvents[15]), exhibiting the characteristics of case II.

Such an explicit dependence on c_1 is cancelled with the analysis involving a plot of $(\phi_{-1})^{-1}$ *vs.* $(c_1)^{-1}$. However, as a result of the competition between the solvent and **1** for interaction with $^1O_2$ (deactivation or chemical reaction), the kinetic rate laws, the apparent kinetic solvent H/D isotope effect $\rho_{D,H}$ and the efficiency of photooxygenation depend characteristically upon c_1 (in accord with *Eqn. 16* and *19*).

On the other hand, the kinetics of the photooxygenation **1** → **2** is not markedly influenced even by considerable concentrations of the photoproduct **2** in the solution: in a control experiment with $CDCl_3$ as solvent, the presence of **2** ($c_2 = 1.5 \cdot 10^{-3}$ mol/l) did not result in a decreased rate of photooxygenation of **1** (initial concentration $c_1 \approx 1.5 \cdot 10^{-3}$ mol/l; irradiation at 710 nm).

Effect of 9,10-Dimethylanthracene (9,10-DMA). Efficient chemical '$^1O_2$-traps' are useful [24] [25] [30] to monitor the rate of generation and the fate of $^1O_2$ in solution (*e.g.* to obtain $\Phi_{^1O_2}$ for photochemically generated $^1O_2$). At the same time, by rapid and specific reaction with $^1O_2$, they act as inhibitors of the photooxygenation of other, less reactive $^1O_2$-substrates, *e.g.* such as **1**, allowing to demonstrate the intermediacy of $^1O_2$ in the (photo)oxygenation reaction.

Of the anthracene derivatives suitable for such a purpose [31], 9,10-dimethylanthracene (9,10-DMA) was selected, since it reacts rapidly with $^1O_2$ ($k_r = 2.1 \cdot 10^7$ l/mol · s in benzene [25]) to give 9,10-dimethylanthracene-9,10-endoperoxide (9,10-$DMAO_2$), but does not quench $^1O_2$ 'physically' to a significant extent [12] [25]. Also, the excited states of anthracene derivatives related to 9,10-DMA are situated

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13) In this case mainly $^1O_2$-deactivation by solvent.

14) In this case, the lifetime of $^1O_2$ in solution is limited mainly by the deactivation of $^1O_2$ by **1**.

15) Correspondingly, for the same solution when studied for the situation with $OD^{710} < 0.2$ (simply by using 1-mm instead of 1-cm cells), the concentration dependence of the rate of photooxygenation of **1** was increased by one order, as expected in the basis of *Eqn. 9* and *12*. Thus, in CCl_4, first-order kinetics were observed for $c_1 \approx 1.5 \cdot 10^{-4}$ mol/l (see *Fig. 1*), while at the same concentration of c_1, second-order kinetics with respect to **1** resulted for the nondeuteriated solvents, in accord with the kinetic scheme for a self-sensitized photooxygenation of **1** involving $^1O_2$.

at a sufficiently high energy to make it an unlikely competitor for $^3O_2$ in a rapid transfer of electronic energy from photoexcited **1**[16]).

On this basis, we made use of the '$^1O_2$-trap' 9,10-DMA by measuring its rate of disappearance in a photooxygenation sensitized by **1** to determine $\Phi_{^1O_2}$ indirectly in the solvents $CHCl_3$, $CDCl_3$, C_6H_6, C_6D_6 and CD_3OD. Illumination of solutions of 9,10-DMA ($c_A = 6.3 \cdot 10^{-3}$ mol/l) and of **1** ($c_1 = 1.44 \cdot 10^{-4}$ mol/l) in $CHCl_3$, saturated with O_2 at 1 atm (s. *Exper. Part*), with monochromatic light of $\lambda = 710$ nm lead to no visible colour change of the solution (**1** was not noticeably photooxygenated under these conditions). Instead, a rapid consumption of the anthracene derivative occurred proceeding at nearly constant rate (*i.e.* nearly independent of c_A) as long as $c_A \gtrsim 10^{-3}$ mol/l, as estimated from the absorption spectrum of the solutions (at $\lambda = 380$ nm). Only after 9,10-DMA had been consumed by oxygenation (to 9,10-DMAO_2) so that $c_A \lesssim 5 \cdot 10^{-4}$ mol/l, the photooxygenation of **1** became noticeably fast and soon after proceeded at a rate, which was not significantly different from that in the beginning of a control experiment, where DMA had not been added to the solution. Evidently, 9,10-DMA protected **1** from photooxygenation (s. *Fig. 6*).

In a second experiment under identical conditions, but $CHCl_3$ replaced by $CDCl_3$ as solvent, again a nearly concentration-independent rate of disappearance

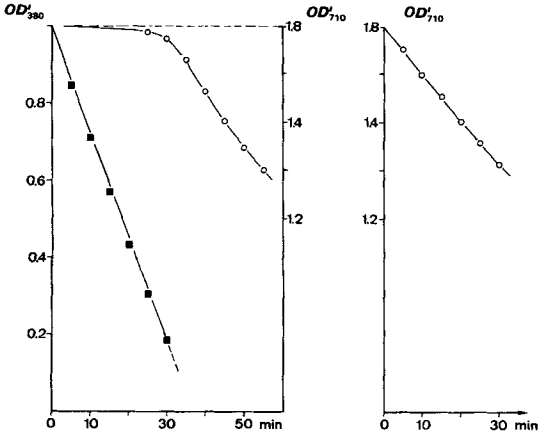

Fig. 6. *Changes of the Optical Densities at 380 nm (OD'380) and at 710 nm (OD'710) Observed during the Photooxygenation of* **1** *in $CHCl_3$ in the Presence* (left; *initial concentration of 9,10-DMA: $6.3 \cdot 10^{-3}$ mol/l) and in the Absence* (right) *of 9,10-DMA.* Wavelength of exciting light: 710 nm; initial concentration of **1**: $1.5 \cdot 10^{-4}$ mol/l; O_2 (1 atm); 20±2°; 1-cm path length; s. *Exper. Part* for details.

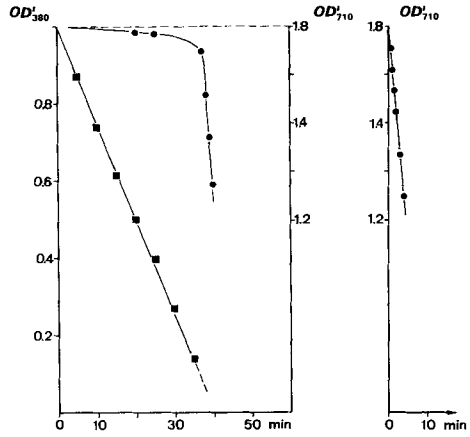

Fig. 7. *Changes of the Optical Densities at 380 nm (OD'380) and at 710 nm (OD'710) Observed during Photooxygenation of* **1** *in $CDCl_3$ in the Presence* (left) *and in the Absence* (right) *of 9,10-DMA.* Exper. conditions, s. *Fig. 6* and *Exper. Part.*

[16]) Energy of S_1 of 9,10-DMA 71.8 kcal/mol, and of T_1 of 9,10-diphenylanthracene 41.8 kcal/mol (in 'nonpolar' solvent [49]).

of 9,10-DMA was observed (as long as $c_A \gtrsim 5 \cdot 10^{-4}$ mol/l), proceeding at a rate barely slower than in the preceding experiment. Only after DMA had mostly been consumed, the photooxygenation of **1** set in, at a rate nearly 10 times faster compared to the run with $CHCl_3$ as solvent, but not noticeably different from the control experiment in $CDCl_3$ without 9,10-DMA (s. *Fig. 7*).

The rate of photooxygenation of 9,10-DMA photosensitized by **1**, apparently, does not respond to the H/D-isotopic composition of the chloroform solutions, as long as the concentration of the anthracene derivative is sufficiently large, indicating $\Phi^H_{^1O_2} \approx \Phi^D_{^1O_2}$ for these solvents. This result is in agreement with the corresponding conclusion drawn form the common intercept of the $(\phi_{-1})^{-1}$ *vs.* $(c_1)^{-1}$ plots. Of course, $\rho_{D,H}$ for the photooxygenation of **1** depends upon the H/D-isotope composition of the solvent, as discussed before.

Similar experiments with C_6H_6/C_6D_6 and CD_3OD as solvents showed the rate of photooxygenation of 9,10-DMA (*i.e.* $\Phi_{^1O_2}$) not only to be insensitive to the H/D-isotopic composition of the solvent, but apparently also to depend only to a small extent on its chemical nature[17]).

To provide additional evidence that under such photooxygenation conditions **1** sensitizes the formation of 9,10-$DMAO_2$ from 9,10-DMA in a clean reaction, preparative experiments were performed as a control. A solution of 9,10-DMA ($9.7 \cdot 10^{-4}$ mol) and **1** ($9.85 \cdot 10^{-8}$ mol) in benzene was saturated with O_2 and irradiated for 160 seconds with filtered light ($\lambda > 550$ nm) of a 150-W W-lamp (s. *Exper. Part*). The photooxygenation product 9,10-$DMAO_2$ was isolated in 93% yield (in the dark) and identified by its ^{1}H-NMR spectrum. Under the same experimental conditions, irradiation of a solution of 9,10-DMA in benzene without **1** for 25 min resulted only in a 5% loss of 9,10-DMA (due to formation of 9,10-$DMAO_2$ mostly, as judged by the ^{1}H-NMR spectrum).

Effect of β-Carotene on the Photooxygenation of **1**. β-Carotene has been shown to be an effective quencher for $^1O_2$ in solution [11a] [32], with a rate approaching the diffusion-controlled limit in various solvents ($k_q^Q \approx (1\text{–}1.5) \cdot 10^{10}$ l/mol · s) [23b]. Quantitative evaluation of quenching experiments with β-carotene, therefore, provides a criterium for the involvement of $^1O_2$ in a photooxygenation reaction in solution. As expected, β-carotene is an excellent inhibitor of the photooxygenation of **1** (s. *Fig. 8*), which, when analyzed quantitatively with the help of *Stern-Vollmer* plots [15], furnishes the quenching constant $(k_q^Q \cdot \tau_s)$ $1.4 \cdot 10^{-6}$ l/mol in $CHCl_3$ and $1.6 \cdot 10^{-7}$ l/mol in $CDCl_3$ (for $c_1 = 1.6 \cdot 10^{-4}$ mol/l). These values allow to estimate the lifetimes τ_s of the oxygenating species to be 60 ± 10 and 520 ± 100 μs in $CHCl_3$- and $CDCl_3$-solutions, respectively; apparently, they are subject to a solvent H/D isotope effect ($\rho_{D,H} = 9.5$) corresponding to $\rho_{D,H}$ for chloroform solutions of **1** at this concentration c_1 (as determined before, the *Table*). This information supports the intermediacy of $^1O_2$ in a quantitative fashion.

Oxygenation of **1** *by* $^1O_2$ *Liberated Thermally from 1,4-Dimethylnaphthalene-1,4-endoperoxide in the Dark.* The correlation of the chemical result of the photo-

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[17]) The crucial solubility of $^3O_2$ in the solvents should be similar when saturated at 1 atm of oxygen at r.t. [36]. The dependence of $\Phi_{^1O_2}$ on c_{O_2}, as expected in view of *Eqn. 14* (s. also [11b]), was not tested experimentally.

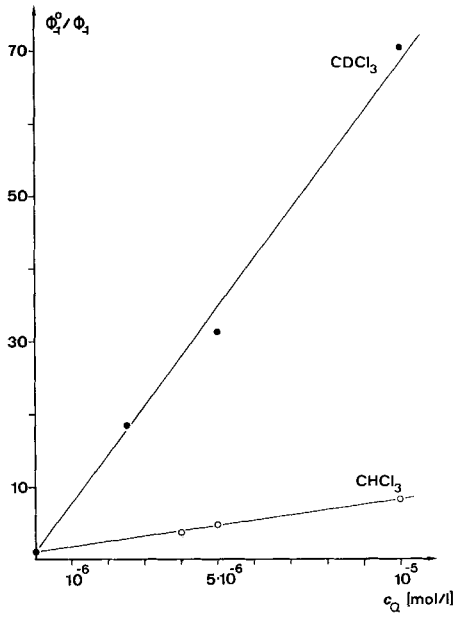

Fig. 8. Stern-Vollmer *Analysis of the Effect of β-Carotene (concentration c_q) on the Rate of Photooxygenation of* **1** *in $CHCl_3$ and in $CDCl_3$, Expressed as the Ratio of the Quantum Yields in the Absence (Φ^0_{-1}) and in the Presence (Φ_{-1}) of the Quencher* [15]. Wavelength of exciting light: 710 nm; initial concentration of **1**: $1.6 \cdot 10^{-4}$ mol/l; $20 \pm 2°$; O_2 (1 atm); path length: 1 cm.

oxygenation with the effect on the photooxygenation substrate of $^1O_2$ generated otherwise in the dark (*e.g.* from thermal decomposition of a suitable oxygenated precursor [33]) allows to interrelate the involvement of $^1O_2$ in these chemical transformations. Qualitatively, this was done by storing a solution of **1** and of a 24-fold molar excess of the thermal $^1O_2$-source 1,4-dimethylnaphthalene-1,4-endoperoxide (1,4-DMNO_2) [31a] [34] in $CDCl_3$ at 34° for 2 h under exclusion of light. Spectral analysis showed 1,4-DMNO_2 to have decomposed to about 30% of its original concentration, with concomitant formation of 1,4-DMN, while workup resulted in isolation of 87% of **2** (identified by ^{1}H-NMR, UV/VIS, and TLC) besides recovery of 10% of **1**[18]). The incomplete conversion of **1** to **2**, in spite of a chemically clean reaction, is compatible with the double function of **1** in the dark with respect to $^1O_2$ as a quencher and as a substrate.

Discussion. The photooxygenation of the Co(III) B-didehydrocobyrinate **1** [7] is found here to follow the kinetic characteristics of a reaction involving 'singlet oxygen' ($^1O_2$) generated *via* photoexcitation of the Co(III)-complex. In this way, evidence for the existence of an (uncharacterized) electronically excited state of **1** is obtained that persists for sufficient time and stores enough electronic energy to generate $^1O_2$ efficiently in aerated or oxygen-saturated solutions.

The activity of the B-didehydrocorrinoid Co(III)-complex **1** as a photosensitizer of reactions involving $^1O_2$, as deduced from the 'photochemical action spectrum'

[18]) Corresponding experiments with CCl_4 as solvent and with storage of **1** and 1,4-DMNO_2 in solutions at r.t. for 14 h resulted in a complete disappearance of **1** and of 1,4-DMNO_2. Compound **2** was obtained in 80% yield (UV/VIS, ^{1}H-NMR, TLC) besides polar, nonidentified side products.

(Fig. 1), contrasts with the inability to find luminescence from photoexcited Co(III)-corrins [2], the subject of search at temperatures down to 4 °K and at wavelengths up to 1000 nm [2]. In view of the luminescence exhibited by metal-free corrins [3] and certain metallocorrins [2], rapid radiationless deactivation of ligand-centered ($\pi\pi^*$) electronically excited states *via* low-lying states involving the central d^6-Co(III)-ion has been made responsible for the lack of luminescence of the Co(III)-corrins [2].

However, in the Co(III)-complex **1** the chromophore of the organic ligand is extended by an additional C,C double bond at the 7,8-position of ring B. Apparently, this causes a significantly different situation, as underlined by a comparison of the UV/VIS-absorption spectra of **1** and of the corrinoid degradation product of vitamin B_{12}, heptamethyl *Co, Coβ*-dicyanocobyrinate (**3**, 'cobester' [9]): *e.g.*, in CH_3OH (containing 0.02% of HCN) the long-wavelength absorption band of **3** exhibits a maximum at 583 nm, while in **1** the corresponding maximum occurs at 707 nm. Therefore, in analogy to the absorption spectra, low-lying ligand-centered electronically excited states of **1** might be shifted to an energy sufficiently low to retard their deactivation *via* the transition-metal ion. Comparison with the absorption spectra of Co(III)-complexes of a series of saturated and partially unsaturated 14- and 15-membered synthetic macrocyclic tetra-amine ligands support such a possibility [35]. Thus, a quantitatively different situation seems to prevail for **1** with respect to the lifetime of low-lying electronically excited states, compared to those of **3** and of other Co(III)-corrins [1][19]).

In this context also, the close correlation of the absorption spectrum of the solution of **1** in CCl_4 with the 'photochemical action spectrum' [17] for the photooxygenation of **1** is of interest *(Fig. 2)*. It indicates $\Phi_{^1O_2}$ (the quantum yield of generation of $^1O_2$) not to be highly sensitive to the wavelength of irradiation[7]). Thus, the central d^6-metal ion Co(III), apparently, does not interfere noticeably in a wavelength-dependent manner. As a consequence, a low-energy electronically excited state of **1**, which presumably is directly responsible for the photosensitized generation of $^1O_2$, seems to be populated with similar efficiency from various higher-lying excited states of **1** (a somewhat analogous situation is found for the photoinduced decomposition of alkylcobalamins in aerated solutions, for which the quantum yields exhibit only a small [1a] (but possibly significant [1c]) dependence on the wavelength of irradiation).

The intermediacy of $^1O_2$ in the self-sensitized photooxygenation of **1** to **2** has been established by examining the effect of the H/D-isotope content of the solvent, the influence of the chemical nature of the solvent, the inhibition by the chemical competitor for $^1O_2$, 9,10-DMA, the retardation by the physical quencher of $^1O_2$,

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[19]) Indeed, in contrast to vitamin B_{12} [1] and other Co(III)-corrins [2], solutions of **1** allow to detect a weak luminescence (even) at r.t. Similarly at 77 °K (in frozen ethanolic solution), photoexcited **1** emits with $\lambda_{max} = 737$ nm, bathochromically shifted by 18 nm compared to the maximum of the long-wavelength absorption band of **1** under these conditions; a second maximum at 810 nm indicates a vibrational fine structure with a spacing of *ca.* 1220 cm^{-1}. The corresponding excitation spectrum of this emission is compatible with the assignment of the emitting species to photoexcited **1** (measurements performed in collaboration with *F. Burkhalter* (group of Prof. Dr. *U. Wild*) at the Institute of Physical Chemistry, ETH-Zürich; unpublished results).

β-carotene, and the simulation of the photooxygenation of **1** to **2** with thermally liberated $^1O_2$ from 1,4-DMNO$_2$ in the dark.

While the kinetic information on one hand was used to establish the intermediacy of $^1O_2$ in the photooxygenation of **1** (and in this way to obtain evidence for a short-lived electronically excited state of **1** capable of transferring electronic energy in an intermolecular manner[20]), also some kinetically useful information on the generation and on the fate of $^1O_2$ in this system was obtained.

Based on the measured rate of disappearance of 9,10-DMA due to photooxygenation sensitized by **1**, a quantum yield $\Phi_{^1O_2}$ (of generation of $^1O_2$ sensitized by **1**) was determined indirectly and found to be practically independent of the solvent H/D isotope content (for chloroform and benzene), and not to depend strongly on the chemical nature of the solvent ($\Phi_{^1O_2}^{CD_3OD} = 0.18 \pm 0.04$; $\Phi_{^1O_2}^{CHCl_3} \approx \Phi_{^1O_2}^{CDCl_3} = 0.12 \pm 0.04$; $\Phi_{^1O_2}^{C_6H_6} \approx \Phi_{^1O_2}^{C_6D_6} = 0.13 \pm 0.04$). On the other hand, the efficiency of photooxygenation of **1** exhibits a considerable dependence on the chemical composition of the solvent. This becomes particularly clear by considering the ratios $k_r/k_r + k_q$, that can be obtained from the intercept of the double-reciprocal plots *(Fig. 3–5)*, and that inform on the partitioning between chemical reaction (to give **2**) and physical quenching (to give $^3O_2$ and **1**) upon interaction of $^1O_2$ with **1** in these solvents at room temperature. Whereas an encounter between **1** and $^1O_2$ that removes $^1O_2$ from a methanolic solution also produces **2** with over 60% probability in this solvent, in benzene only about 8% of such interactions lead to formation of 2 (while 92% result in deactivation of $^1O_2$).

Secondly, from the ratio of the slope *vs.* intercept of the double-reciprocal plots $(\phi_{-1})^{-1}$ *vs.* $(c_1)^{-1}$ *(Fig. 4–5)* the ratio $k_s/k_r + k_q$ can be obtained [11]. Consequently and using the published values of k_s [22], the sum of the rates of deactivation of $^1O_2$ by **1** ($k_t = k_r + k_q$) can be evaluated to be $(6 \pm 2) \cdot 10^6$ l/mol · s in methanol, $(8 \pm 1) \cdot 10^6$ l/mol · s in benzene and $(5 \pm 3) \cdot 10^6$ l/mol · s in chloroform, suggesting only little dependence of k_t on solvent chemical and H/D isotopic composition. Furthermore, based on k_s and k_t (calculated this way) the experimentally derived $\rho_{D,H}$ *(Table)* are reproduced well using *Eqn. 19*. This confirms in a quantitative way the interdependence of c_1, $\rho_{D,H}$, and the kinetic rate law for the photooxygenation of **1** in a mechanism involving $^1O_2$.

Such a dependence of the chemical fate of $^1O_2$ on the solvent, when interacting with a $^1O_2$-substrate (little influence of the solvent on k_t (*i.e.* on the total rate of deactivation of $^1O_2$ by **1**), but a pronounced effect on the term $k_r/(k_r + k_q)$ (*i.e.* on the probability of a chemical reaction)) has received attention recently [37a] [37b] and supplements the well-known solvent dependence of the chemical outcome of photooxygenation reactions [38]. Usually, a highly polar intermediate oxygenated species[21]) is inferred from such effects of the solvent polarity and/or availability

[20]) With $c_{O_2} \approx (1\text{–}2) \cdot 10^{-2}$ mol/l, as in most organic solvents when saturated with O_2 at 1 atm [36], quenching by $^3O_2$ (which often proceeds close to diffusion controlled [15] and may result in the formation of $^1O_2$ efficiently [13]) can occur with rates $k_q \approx (2\text{–}6) \cdot 10^8$ s^{-1}. The appearance of photogenerated $^1O_2$ in solution, therefore, can provide evidence for a photosensitizing compound whose electronically excited states are short-lived ($\lesssim 10^{-9}$ s) and may escape observation otherwise.

[21]) A chemically irreversibly formed (*e.g.* [37a]) and a loosely (reversibly) associated oxygen-substrate complex [37b–d] have been proposed as intermediate oxygenated species in reactions of $^1O_2$.

of solvent protons on the course of reactions involving $^1O_2$. The data at hand concerning the photooxygenation **1** → **2** support the interpretation that such intermediate stages occur also in this reaction.

A solvent effect was not noticed, however, regarding the chemical outcome[22]) of the photooxygenation of **1**, which proceedes with a regioselectivity that seems to reflect the reactivity of the ligand π-systems towards electrophilic attack at a single C-center [7][23]) (but presumably is enhanced at C(5) due to relief of strain caused by interaction of CH_3-groups at C(5) and at C(7) in **1**). At a later stage, the reaction might proceed *via* a (5,6)-dioxetane-derived intermediate as precursor to the product **2** (in analogy to the proposed intermediate dioxetanes during photooxygenation reactions of Mg-octaethylporphyrin [39a], of chlorophyll derivatives [39b] [39c] and of various enamines [39d]).

In conclusion, the self-sensitized and efficient photooxygenation of **1** to give **2** regioselectively and in a yield of 96% establishes a new aspect of the photoreactivity of corrinoid Co-complexes. Apparently a significant fraction (even) of the (short-lived) electronically excited **1** can efficiently transfer energy onto molecular oxygen ($^3O_2$) in aerated or oxygen-saturated solutions and promote it to its singlet-excited state ($^1O_2$). $^1O_2$ generated this way, rapidly recombines with **1** to cleave it to **2** regioselectively. Indeed, considerable selectivities in reactions of (natural) 'tetrapyrrolic' pigments with $^1O_2$ are not unique, and photooxygenation reactions have found use as a means to specifically oxygenate (functionalize or degrade) several porphyrins [12b] [39a] [40] [41] and chlorins [39b] [39c] [42]. We have recently introduced vitamin-B_{12} derivatives (containing Co(III)) to this group [10]. However, it seems feasible that the reported but uncharacterized reactions of metal-free [43] and Zn(II)-containing [44] vitamin-B_{12} derivatives to yellow compounds upon exposure to light already constitute an unnoticed precedence for this type of reaction in the field of natural corrinoids.

We are grateful to Prof. Dr. *A. Eschenmoser* for his support of this work and to *F. Hoffmann-La Roche & Co. AG*, Basel, for a scholarship (to *R. S.*). We would like to thank also Prof. Dr. *U. Wild* and *F. Burkhalter* (Institute of Physical Chemistry, ETH Zürich) for their help with the luminescence measurements.

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[22]) Similar kinetic experiments (at $c_1 \approx 1.5 \cdot 10^{-4}$ mol/l) were also performed in CH_3CN and CD_3CN ($\rho_{D,H} \approx 3.8$), in CH_2Cl_2 and CD_2Cl_2 ($\rho_{D,H} \approx 8.4$), and in CH_3COCH_3 and CD_3COCD_3 ($\rho_{D,H} = 5.7$). The relative rates of photooxygenation of **1** in C_6H_6, CH_2Cl_2, CH_3COCH_3, CH_3OH, $CHCl_3$, CH_3CN, CS_2 and in CCl_4 ($c_1 \approx 1.5 \cdot 10^{-4}$ mol/l, r.t., 1 atm O_2, $\lambda_{exc.} = 710$ nm and $OD^{710} > 1.6$) were 0.08, 0.17, 0.17, 0.21, 0.30, 0.58, 1.0, and 3.0, respectively. The conversion **1** → **2** was clean in all these solvents, as judged by reaction isosbestic points in the UV/VIS spectra and by the appearance of a single product by TLC.

[23]) Preliminary experiments with the 'cationic' *Co*-aquo-*Co*-cyano-pyrocebester (obtained as a perchlorate salt by treatment of **1** with dilute perchloric acid as described by *Werthemann* for 'cobester' (**3**) [9b]) show it to be considerably more resistent towards photooxygenation (in oxygen-saturated $CDCl_3$) and towards oxygenation by thermally generated $^1O_2$ (from thermolysis of 1,4-DMNO$_2$ in $CDCl_3$), but a small amount of **2** is found (upon workup[24]) of such reaction solutions).

Experimental Part [45]

1. *General.* Abbreviations: 9,10-DMA, 9,10-dimethylanthracene; 1,4-DMN, 1,4-dimethylnaphthalene; 1,4-$DMNO_2$, 1,4-dimethylnaphthalene-1,4-endoperoxide [34][6]). Reagents and solvents: hexamethyl *Coa,Coβ*-dicyano-7-de(carboxymethyl)-7,8-didehydrocobyrinate ('pyrocobester', **1**): prepared in analogy to the method of *Inhoffen et al.* [6], crystallized and recrystallized from methyl acetate/hexane, m.p. 210–211° ([6]: 150–155°), identified by TLC, UV/VIS and ^{1}H-NMR; CH_3OH: *Fluka, puriss., p.a.,* distilled at 1 atm; CH_3OD: *Fluka, puriss.,* > 99.9% D, distilled at 1 atm; CD_3OD: *Fluka, puriss.,* > 99.8% D, distilled at 1 atm; $CHCl_3$: *Fluka, puriss., p.a.*, distilled at 1 atm and filtered through basic aluminum oxide; $CDCl_3$: *Fluka, puriss.,* > 99.8% D, same purification as for $CHCl_3$; C_6H_6: *Fluka, puriss., p.a.,* distilled at 1 atm; C_6D_6: *Fluka, puriss.,* > 99.5% D, same purification as for C_6H_6; CH_2Cl_2: *Fluka, puriss., p.a.,* distilled from P_2O_5 at 1 atm and filtered through basic aluminum oxide; CD_2Cl_2: *Fluka, puriss.,* > 99.5% D, same treatment as for CH_2Cl_2; CH_3CN: *Fluka, puriss., p.a.;* CD_3CN: *Fluka, puriss.,* > 99.8% D; CH_3COCH_3: *Fluka, puriss., p.a.;* CD_3COCD_3: *Fluka, puriss.,* > 99.5% D; CS_2: *Merck, p.a.;* CCl_4: *Merck, p.a.,* distilled at 1 atm; aluminum oxide: alumina basic, act. I, *Woelm 02069;* 9,10-DMA: *Fluka, purum,* sublimed before use (100°, high vacuum); oxygen: *Stickstoff-Wasserstoffwerke,* Luzern; β-carotene: *Fluka, purum,* > 98%, checked spectrophotometrically in hexane ($\log\varepsilon_{452} = 5.12$; [50]: $\log\varepsilon_{452} = 5.14$); $K[Cr(NH_3)_2(SCN)_4]$ (*Reinecke's* salt): prepared from $NH_3[Cr(NH_3)_2(SCN)_4]$ *(Fluka, purum)* by the procedure of *Wegner & Adamson* [48]. TLC plates coated with silica gel *60, Merck* Art. 5271. ^{1}H-NMR: *Bruker WM-300* (300.14 MHz) or *Bruker WP-80* (80 MHz); in $CDCl_3$; TMS internal reference, chemical shifts in ppm with $\delta(TMS) = 0$.

2. *Apparatus.* For kinetic experiments, the irradiations were conducted using a 1600-W Xe high-pressure lamp *(Osram XBO 1600),* operated at 1000 W, a grating monochromator[25]) fitted with an *Echelette* grating (*Bausch & Lomb,* No. *2SM 211 R*), a beam splitter (Quartz *Suprasil, I 60×2, Haraeus Schott*) and a thermostated cell holder. Actinometry with *Reinecke's* salt [48] and/or a quantum-flux meter built by Dr. *W. Heinzelmann*[25]) were used to monitor the light intensity; for measurements in the wavelength range 400–600 nm, a filter (*KV 370, Jenaer Glaswerke, Schott & Gen.,* Mainz) was used to eliminate the 2nd-order spectrum, and, in addition, an aq. $Na_2CO_3/Na_2Cr_2O_7$ solution [49] was used for irradiations above 600 nm. The monochromator was calibrated with the Hg- and the Na-lights of an *Oriel* spectral calibrations set (*Oriel,* Stanford, Conn., USA). The xenon lamp was run with a power supply *Heinzinger TNX 1600* and an ignition device *Bauch* No. *2500.* A *Perkin-Elmer* double beam grating spectrophotometer *(PE-124)* and a *W+W 1100* recorder were used to record the UV/VIS-absorption spectra.

3. *Experimental Procedures.* – 3.1. *Determination of the 'Photochemical Action Spectrum'*[24]). Of an O_2-saturated stock solution of 'pyrocobester' (**1**) in CCl_4 ($c_1 = 1.56 \cdot 10^{-4}$ mol/l), 300 µl were transferred into a 1-mm-quartzabsorption cell under O_2, an absorption spectrum was taken, and then the cell was placed into the thermostated (20±2°) cell holder of the irradiation apparatus. Then, the sample cells were exposed to monochromatic irradiations at 350, 370, 400, 416, 452, 550, 600, 650, 690, 710, 730, 760, or 800 nm (and, when necessary, using the filters as described above) for (usually) 4 time intervals of 30 sec (or 1 min). The changes of the content of the sample cells were determined spectrophotometrically and the rate of disappearance of **1** determined (using 1st-order kinetics with respect to **1**). The light intensity of the irradiation system at 316, 350, 392, 416, 452, 504, 520, 545, 600, 676, and 713 nm and at the location of the sample cell was determined by actinometry using *Reinecke's* salt $K[Cr(NH_3)_2(NCS)_4]$ following the procedure of *Wegner & Adamson* [48]. The wavelength dependence of the light intensity of the irradiation apparatus followed well the pattern determined earlier [46] [47] for the wavelength range 310–713 nm (with an increasing scatter of the experimental values (*ca.* ±10%) at the long wavelengths (676 and 713 nm); a constant value was used for the light intensity at 720–800 nm, as given by the manufacturer). The 'photochemical action spectrum' for the photooxygenation **1**→**2** in CCl_4 was then established based on the values of the rates of disappearance of **1**, which were corrected for the actual OD^λ of the solution and for the wavelength dependence of the light intensity of the irradiation system. The spectrum of *Figure 2* is based on a

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[24]) All manipulations of light-sensitive compounds were done in a dark room with low light exposure.

[25]) The irradiation apparatus was built under the supervision of Dr. *W. Heinzelmann* at the Institute of Physical Chemistry, University of Zürich, and is described in [46] [47].

calibration point at 690 nm. The stability of the light intensity of the irradiation system was monitored routinely at 550 nm with the help of the quantum-flux meter.

3.2. *Procedure for Irradiation Experiments for Kinetic Analyses*[24]). A weighed amount of crystalline **1** was dissolved in a small amount of one of the specified solvents, and the sample was diluted to a calibrated volume of the solution, which then was saturated with O_2 (at 1 atm). Then, 3.0 ml (0.30 ml) of the O_2-saturated solution were transferred into a 1-cm (0.1-cm) quarz absorption cell (filled with O_2) and the cell was stoppered tightly after O_2 gas was bubbled through the solution carefully for additional 30 sec (15 sec). The amount of **1** in the sample cell at the outset of the experiment was determined by recording an absorption spectrum of the solution (it was chosen to result in an OD^{710} of either 1.7–1.9 or of 0.15–0.20), and then, the cell containing the test solution was placed into the thermostated cell holder (at $20\pm2°$) of the irradiation system. The sample was submitted to irradiation (in general at 710 nm) for a preselected length of time, shaken to mix the content of the cell, and a second absorption spectrum was run to determine the extent of the photoreaction. This procedure was repeated several times till the desired amount of **1** (usually about 50%) had been consumed by photooxygenation. Analysis by TLC at the end of each series was used to check the uniformity of the reaction.

3.3. *Photooxygenation of* **1** *in the Presence of 9,10-DMA*[24]). The procedure in these experiments was similar to the one described in *Sect. 3.2.* A weighed amount of 9,10-DMA was added to the solutions of **1** ($c_1 \approx 1.5 \cdot 10^{-4}$ mol/l; 3 ml, 1-cm absorption cell) to give a typical concentration $c_A \approx 6.3 \cdot 10^{-3}$ mol/l at the beginning of the irradiations. To determine the rate of disappearance of 9,10-DMA (monitored as long as $c_A \gtrsim 5 \cdot 10^{-4}$ mol/l), 50 µl of the sample solution were withdrawn at the beginning of the irradiation and after regular time intervals of illumination at 710 nm (the sample cell was opened under O_2 atmosphere). These samples were diluted to 3.0 ml in a 1-cm absorption cell, and the absorption spectrum was run (300–800 nm). Care was taken (particularly) in these experiments to mix the sample solutions at short time intervals, if needed, to avoid local exhaustive depletion of photooxygenation substrate due to nonuniform irradiation intensity. The small loss of solution volume, due to the samples removed (about 300 µl in total), was taken into consideration for the numerical evaluation of the data (*Fig. 6* and *7*).

3.4. *Quenching Experiments with β-Carotene*[24]). The procedure was similar to the one described in *Sect. 3.1* ($c_1 = 1.6 \cdot 10^{-4}$ mol/l in 3 ml of $CHCl_3$ or $CDCl_3$ at the beginning of the experiments, 1-cm absorption cells). A known amount of β-carotene (from a freshly prepared stock solution in freshly purified solvent) was added to the sample solution and the concentration of β-carotene checked spectrophotometrically. Irradiation at 710 nm and observation of the depletion of **1** were done as described above; β-carotene was found to be degraded slightly (less than 10%) during these photooxygenation experiments.

3.5. *Preparative Photooxygenation of 9,10-DMA Using* **1** *as Photosensitizer*[24]). The 9,10-DMA (200 mg, 97 µmol) and **1** (0.1 mg, 0.1 µmol) were dissolved in C_6H_6 (3 ml), and the green solution was transferred into a *Schreiber* photoreactor (see *Fig. 2* in [10]; with a 2-mm spacing for the reaction solution). The solution was purged with O_2 for 5 min, and, while continuing the O_2 bubbling, the photoreactor was placed into a beaker containing cooled H_2O (at about 15°). The solution was irradiated with a 15-V/150-W W-lamp (*General Electric*, type *EFR*), situated at twice the focal length of the lamp mirror and using an aq. $Na_2Cr_2O_7$ filter (2 cm, 1 g $Na_2Cr_2O_7$/l) to eliminate light of $\lambda < 550$ nm. The disappearance of 9,10-DMA was followed spectrophotometrically (and by TLC), and the photooxygenation was stopped after 160 sec. The solvent of the green solution was evaporated at reduced pressure in the dark, and after drying (r.t., high vacuum), the ^{1}H-NMR of the residual solid (21.5 mg) in $CDCl_3$ indicated a clean conversion of 9,10-DMA to *9,10-epidioxy-9,10-dimethyl-9,10-dihydroanthracene* (9,10-$DMAO_2$). – ^{1}H-NMR (80 MHz): 2.15 (*s*, 6 H); 7.1–7.6 (*m*, 8 H).

In a control experiment (in the absence of **1**, 25 min irradiation), ^{1}H-NMR and TLC showed the reisolated solid (recovered in 99%) to consist of 9,10-DMA with only about 4% conversion to 9,10-$DMAO_2$.

3.6. *Thermolysis of 1,4-DMNO$_2$ in a Solution of* **1** *in CDCl$_3$*[18])[24]). A solution of 46 mg of 1,4-$DMNO_2$ (244 µmol, prepared by the method of *Wassermann & Larson* [34] and checked by ^{1}H-NMR: residual 1,4-DMN <4%) and of 10.0 mg (9.8 µmol) of **1** in 350 µl of $CDCl_3$ was stored in the dark at 34° in an NMR tube. The course of the reaction was followed by ^{1}H-NMR, and after 2 h, when the reaction was stopped, *ca.* 70% of 1,4-$DMNO_2$ was converted to 1,4-DMN. TLC

(CH_2Cl_2/CH_3OH (+ 1% HCN) 96:4) supported extensive oxygenation **1**→**2**, with minute amounts of side products. Transfer of the mixture onto a TLC plate and workup as described in [7][24]) lead to 8.9 mg (8.5 μmol, 87%) of **2** besides 1.0 mg (1 μmol) of **1**, both identified by ^{1}H-NMR and UV/VIS [6] [7] as well as by TLC.

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