systems. It should be stressed that the ICDH used in the present study contained no NADP$^+$, as judged from the lack of its characteristic UV absorption spectrum. Willner et al.[7] accomplished the same fixation reaction by using a photosensitized NADPH regeneration system. In this case Ru(bpy)$_3^{2+}$ was used as a photosensitizer, *d,l*-dithiothreitol as an electron donor, and ferredoxin-NADP$^+$ reductase as an enzyme to recycle NADPH. The conversion efficiencies were relatively low (4.6%). Secondly, the potential at which efficient CO$_2$ fixation has been accomplished is the least negative reported to date. Frese et al.[3c] previously reduced CO$_2$ at Ru electrodes in aqueous solutions (pH 3) at −0.35 V vs SCE. However, current efficiencies were less than 1%. Finally, the results obtained in this study suggest that a variety of CO$_2$ fixation reactions may be developed by using enzymes that are involved in vivo CO$_2$-related metabolic pathways as electrocatalysts.

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Quenching of Naphthalocyanine Triplets by O$_2$: Application of the Sandros Equation

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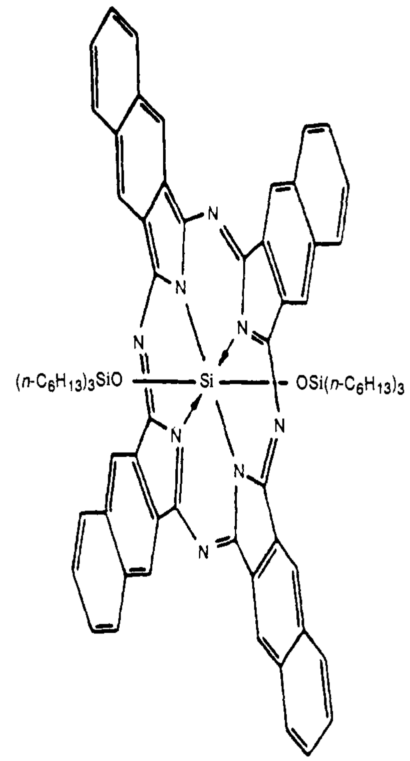
Recently we showed that the triplet (T$_1$) energy of bis(tri-*n*-hexylsiloxy)silicon 2,3-naphthalocyanine (SiNc, see below) is 1.0 kcal/mol lower than that of singlet molecular oxygen (22.5 kcal/mol).[1] Sandros[2] showed that for endergonic triplet energy transfer reactions the bimolecular rate constant decreases nearly exponentially with increasing energy gap between the donor and the acceptor.[3] Thus, small variations in the triplet energies of metal 2,3-naphthalocyanines caused by changes in the nature of the metal and solvent are expected to have a significant effect on the efficiency of triplet quenching by O$_2$. Further, if the S$_1$–T$_1$ energy gap (E_{ST}) remains constant within the 2,3-naphthalocyanine family, then the quenching rate constant should be related by the Sandros equation to the energy of the S$_0$–S$_1$ transition. The results described below show that the predicted relationship is obeyed with $E_{\mathrm{ST}} = 15.6 \pm 0.4$ kcal/mol, in agreement with the value determined spectroscopically for SiNc.[1] This is the first example of the application of the Sandros equation to triplet quenching by O$_2$ and the first to correlate triplet energy transfer kinetics with singlet energy levels.

The Sandros equation[2] relates the bimolecular rate constant for triplet–triplet energy transfer (k_{TT}) between a donor (D) and an acceptor (A) to the diffusion-controlled rate constant (k_{diff}) and the difference in the triplet energies (E_{T}) of D and A (eq 1).



In the case of energy transfer from a donor triplet to O$_2$ ($^3\Sigma_g^-$) to produce O$_2$ ($^1\Delta_g$) (energy requirement $E_\Delta = 22.5$ kcal/mol), a factor of one-ninth has to be introduced into the expression for the bimolecular rate constant ($k_{\mathrm{T}\Sigma}$) because only one-ninth of the intervening collision complexes are of overall singlet multiplicity (eq 2). We can replace E_{T} by the difference between the singlet S$_1$ energy (E_{S}) and the S$_1$–T$_1$ energy gap (E_{ST}), so that the expression for $k_{\mathrm{T}\Sigma}$ becomes eq 3.

$$k_{\mathrm{TT}} = k_{\mathrm{diff}}/(1 + \exp(-(E_{\mathrm{T}}^{\mathrm{D}} - E_{\mathrm{T}}^{\mathrm{A}})/RT)) \qquad (1)$$

$$k_{\mathrm{T}\Sigma} = (^1/_9)k_{\mathrm{diff}}/(1 + \exp(-(E_{\mathrm{T}} - E_{\Delta})/RT)) \qquad (2)$$

$$k_{\mathrm{T}\Sigma} = (^1/_9)k_{\mathrm{diff}}/(1 + \exp(-(E_{\mathrm{S}} - E_{\mathrm{ST}} - E_{\Delta})/RT)) \qquad (3)$$

A variety of solvents were used in these experiments, so we chose to use 2′-acetonaphthone (An) as a reference compound to compensate for the effects of the solvent dependencies of k_{diff} and O$_2$ solubility. The triplet energy of An (59 kcal/mol) is sufficiently greater than E_Δ that the exponential term in eq 2 is negligible, giving $k_{\mathrm{T}\Sigma}^{\mathrm{An}} = (^1/_9)k_{\mathrm{diff}}$.[4] Thus, the relative values of $k_{\mathrm{T}\Sigma}$ of a naphthalocyanine (Nc) and An in any particular solvent obey eq 4.

$$k_{\mathrm{T}\Sigma}^{\mathrm{Nc}}/k_{\mathrm{T}\Sigma}^{\mathrm{An}} = 1/(1 + \exp(-(E_{\mathrm{S}} - E_{\mathrm{ST}} - E_{\Delta})/RT)) \qquad (4)$$

The naphthalocyanine triplets decayed biexponentially in air- and O$_2$-saturated solutions due to reversible energy transfer[1] and two decay components were clearly resolvable in most cases. The measured rate of the early component (γ_1) has the analytical form given in eq 5, where $k_{\Delta\mathrm{G}}$ represents the bimolecular rate constant

$$\gamma_1 = k_{\mathrm{T}\Sigma}[\mathrm{O}_2] + k_{\Delta\mathrm{G}}[\mathrm{Nc}] \qquad (5)$$

for energy transfer from O$_2$ ($^1\Delta_g$) to ground-state naphthalocyanine.[1] Values of $k_{\mathrm{T}\Sigma}^{\mathrm{Nc}}$ were thus obtained from the dependence of γ_1 on the percent of O$_2$ in the saturating gas (21% or 100%).

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(3) This dependence of rate constant on energy gap was demonstrated concurrently by Stevens and Walker (Stevens, B.; Walker, M. S. *Proc. Roy. Soc.* **1964**, 26, 27, 109).

(4) Based on an O$_2$ concentration in air-saturated benzene of 1.9×10^{-3} M,[5] the absolute value of $k_{\mathrm{T}\Sigma}$ for An in benzene was $(1.5 \pm 0.1) \times 10^9$ M^{-1} s^{-1}, which is in agreement with the value expected on the basis of $k_{\mathrm{diff}} = (1\text{–}2) \times 10^{10}$ M^{-1} s^{-1}.[6,7] The triplet states of An and the naphthalocyanines were produced and monitored by laser flash photolysis with 355 nm (≈10 ns) light pulses from a Q-switched Nd:YAG laser for excitation. Monitoring wavelengths were 425–430 nm for An and 580–600 nm for Nc.

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Table I. Absorption Maxima, Singlet State Energies, and Relative Rate Constants for Triplet Quenching by $O_2(^3\Sigma_g^-)$ of Trihexylsiloxymetal 2,3-Naphthalocyanines and Trihexylsiloxysilicon 2/3-Tetrahalo-2,3-naphthalocyanines in Various Solvents (25 °C)

no.	metal[a]	halogen	solvent[b]	λ_{max}[c] (nm)	E_S[d] (kcal/mol)	$k_{T\Sigma}^{Nc}/k_{T\Sigma}^{An}$[e]
1	Al		DMA	754	37.8	0.43
2	Ga		DMA[f]	765	37.3	0.11
3	Si		C_6H_{12}	767	37.2	0.20
4	Si	Cl	TMB	774	36.8	0.20
5	Si		C_6H_6	775	36.8	0.13
6	Si		TMB	776	36.8	0.14
7	Si	Br	TMB	776	36.8	0.20
8	Al		Py	776	36.7	0.069
9	Si		DMA	777	36.7	0.068
10	Sn		C_6H_{12}	778	36.7	0.041
11	Sn		C_6H_6	788	36.2	0.030
12	Ga		C_6D_6[f]	794	35.9	0.024
13	Ga		TMB	795	35.9	0.021
14	Al		TMB	796	35.8	0.017
15	Sn		TMB	797	35.8	0.019

[a] The Al and Ga naphthalocyanines carry one trihexylsiloxy group as an axial ligand, while the Si and Sn naphthalocyanines carry two *trans*-trihexylsiloxy groups. [b] Abbreviations: DMA = *N,N*-dimethylacetamide, C_6H_{12} = cyclohexane, TMB = 1,2,4-trimethylbenzene, Py = pyridine. [c] *Q*-band absorption maximum; ±0.5 nm. [d] ±0.1 kcal/mol. [e] ±10% except for no. 1 (±20%). [f] Solution contained 5–8 mM of either sodium azide (in DMA) or 1,4-diazabicyclo[2.2.2]octane (in TMB).

When the two triplet decay components were not clearly resolvable, a singlet oxygen quencher (either sodium azide or 1,4-diazabicyclo[2.2.2]octane) was added to make the decay exponential. Separate experiments in which both components of the triplet decay were resolvable verified that this quenching technique was valid. Further, the possibility[8] that electron transfer from the triplet to O_2 ($^3\Sigma_g^-$) occurred in the most polar solvent employed, *N,N*-dimethylacetamide, was ruled out by the absence of residual transients following the decay of the triplet.[9]

The naphthalocyanines and solvent systems examined are listed in Table I.[13] The peak position of the lowest energy absorption band (λ_{max}) depended on solvent for all the naphthalocyanines, but the greatest range of band maxima was obtained with AlNcOSi(n-C_6H_{13})$_3$ (Table I, Figure 1 (inset)). The singlet energy (E_S) is usually taken to be midway between the energies of the 0,0 transitions in the absorption and fluorescence spectra: $E_S = (^1/_2)(E_{max}^{abs} + E_{max}^{fl})$. The fluorescence spectra of the naphthalocyanines mirrored the absorption, and the Stokes shifts between the 0,0 band maxima were in the range 2–6 nm (0.1–0.3 kcal/mol). For simplicity, an average Stokes shift of 0.2 kcal/mol was assumed for all solutions. The values of E_S were thus obtained by subtracting 0.1 kcal/mol from E_{max}^{abs}. Figure 1 shows the plot of the data in the last column of Table I vs E_S. The theoretical curve in this plot was obtained from eq 4 with E_{ST} = 15.6 kcal/mol. The data points fall within the limits determined by E_{ST} = 15.6 ± 0.4 kcal/mol, which is in agreement with the value determined spectroscopically for SiNc (E_{ST} = 15.4 kcal/mol).[1] We conclude that the fact that the Sandros equation relates the T_1 quenching constants of the naphthalocyanines to their S_1 energies arises because the S_1–T_1 energy gap is determined primarily by the ring skeleton and is not significantly influenced by the central metals or solvents examined.

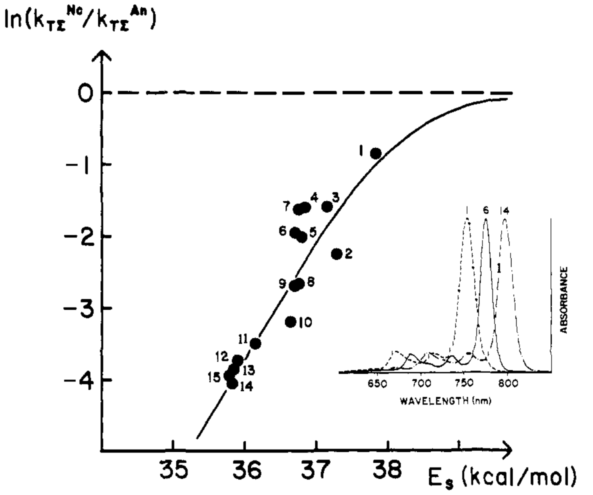

Figure 1. Dependence of rate constant for Nc triplet quenching by O_2 on the naphthalocyanine singlet excited state energy. The rate constants for the naphthalocyanines are relative values compared to the rate constant for quenching of the triplet of 2′-acetonaphthone in the same solvent. The experimental points are numbered according to the sequence in Table I. The theoretical line is calculated according to eq 4 with E_{ST} = 15.6 kcal/mol (E_Δ = 22.5 kcal/mol). Inset: representative absorption spectra of AlNcOSi(n-C_6H_{13})$_3$ in DMA (no. 1), SiNc(OSi(n-C_6H_{13})$_3$)$_2$ in TMB (no. 6), and AlNcOSi(n-C_6H_{13})$_3$ in TMB (no. 14) normalized to the same relative maximal absorbance.

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(8) We acknowledge a referee for raising this question.

(9) No long-lived (>5 μs) transients absorbing in the wavelength range 450–670 nm were observed in an O_2-saturated solution of SiNc(OSi(n-C_6H_{13})$_3$)$_2$ in *N,N*-dimethylacetamide containing NaN_3 (8 mM) following the decay of the triplet state. On the basis of the approximate reduction potentials (vs NHE) of SiNc(OSi(n-C_6H_{13})$_3$)$_2$ (SiNc$^{\bullet+}$/SiNc, $E° \approx +0.8$ V)[10] and azide ion ($N_3^\bullet/N_3^-$, $E° \approx +1.3$ V),[11] azide ion should not reduce the naphthalocyanine radical cation, which would be produced if electron transfer to O_2 ($^3\Sigma_g^-$) occurred. Thus, we conclude that electron transfer can be neglected as a triplet quenching mechanism. Moreover, the triplet state of SiNc(OSi(n-C_6H_{13})$_3$)$_2$ is estimated to have a reduction potential $E° \approx -0.1$ V, which is 0.5 V more positive than the potential required to reduce O_2 to $O_2^{\bullet-}$ in this solvent.[12]

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(13) A synthesis of SiNc(OSi(n-C_6H_{13})$_3$)$_2$ has been given earlier.[10] Syntheses of the remaining compounds will be given in subsequent papers.

A Stereoselective Synthesis of Functionalized Alkenyllithiums and Alkenyl Cyanocuprates by the Cu(I)-Catalyzed Coupling of Organolithium Reagents with α-Lithiated Cyclic Enol Ethers

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The α-metalation of cyclic enol ethers with organolithium reagents is a clean and efficient process which has been extensively exploited in synthesis.[1,2] Far less familiar are the reactions of

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