The enhancement by visible light of the catalytic activity of Co(II)-tetrasulphophthalocyanine on the oxidation of mercapto-ethanol

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CH_3I affords *Z,Z*-6. The configurational stability of 5 appeared in a separate experiment: cleavage of *Z,Z*-6 (prepared from $\text{Z-CH}_3\text{S-C}\equiv\text{C-CH=CH-CH}_3$ and $\text{LiAlH}_4 \cdot \text{CuBr}$ in a THF/HMPT mixture, compare ref. 6) by sodium in liquid ammonia or THF/HMPT, followed by methylation, gave *Z,Z*-6 in about 90% yield.

It is remarkable that the stereochemistry of the cleavage of 1 strongly depends upon the nature of the cleavage reagent: Na-naphthalene or Na in THF/HMPT with *t*-C₄H₉OH as proton donor. A possible explanation for the difference in stereochemistry is that in the absence of a proton donor with sufficient kinetic acidity rotation around the C(3)-C(4) bond in the di-anion 2 can occur, with formation of the 1*Z*,3*E*-di-anion. In any case it can be concluded from our experiments that the mono-methylation and -protonation of the di-anion 2 (irrespective of its configuration) occurs preferentially on the terminal carbon atom. These results

stand in strong contrast to those obtained from the methylation and protonation of the mono-anion $\text{CH}_3\text{S-CH=CH-CH-CH-CH}_2$ prepared from $\text{CH}_3\text{S-CH=CH-CH=CH-CH}_3$ and strong bases like KNH_2 in liquid NH_3 ³, or $\text{LiN(i-C}_3\text{H}_7)_2$ in THF. In these cases the predominant products (>90 rel. %) are $\text{CH}_3\text{S-CH=CH-CH(CH}_3\text{)CH=CH}_2$ and $\text{CH}_3\text{S-CH}_2\text{CH=CH-CH=CH}_2$, respectively.

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THE ENHANCEMENT BY VISIBLE LIGHT OF THE CATALYTIC ACTIVITY OF Co(II)-TETRASULPHOPHTHALOCYANINE ON THE OXIDATION OF MERCAPTO-ETHANOL

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Abstract. The rate of the selective oxidation of mercaptoethanol by dioxygen to disulphide, catalysed by Co(II)-tetrasulphophthalocyanine, is enhanced with a factor 2 à 4 by irradiation with light in the range of 600-700 nm. This effect can be ascribed to the conversion of dimers of Co(II)-tetrasulphophthalocyanine to catalytically active monomers.

In recent publications many new aspects of the photochemistry of phthalocyanines are reported¹ and especially in photo-electrochemistry the irradiation with visible light of electrodes with a surface layer of phthalocyanines may have a remarkable effect². Phthalocyanines are also very effective catalysts, especially in the homogeneous oxidation of mercaptans by dioxygen^{3,4}, but hitherto no reports have been published concerning the influence of light when using these systems as catalysts.

In our laboratory the effect of phthalocyanines on the oxidation of mercaptoethanol at room temperature was studied: $4\text{RSH} + \text{O}_2 \rightarrow 2\text{RSSR}$ with $\text{R} = -\text{CH}_2-\text{CH}_2\text{OH}$.

In a typical experiment a 80 ml reaction mixture consisting of 6 mmol NaOH, 0.05 μmol CoTSP (TSP = tetrasulphophthalocyanine-ion; counterions are 4 Na^+), 14 mmol RSH and water, in a Warburg apparatus absorbed O_2 at a rate of 17 mol O_2 (mol cat.) $^{-1}\text{s}^{-1}$. Irradiation with a Philips halogen lamp type 7158 caused an increase to a rate of 54 mol O_2 (mol cat.) $^{-1}\text{s}^{-1}$. Interruption of the light beam restored the original activity. This cycle could be repeated several times. No light effect could be observed in the absence of CoTSP.

Although the reactor was thermostated and protected with a waterbath to avoid heating by the lamp, a rise of the temperature with $\pm 2^\circ\text{C}$ (measured inside the reactor) was unavoidable. However, experiments carried out in the range of $10\text{--}35^\circ\text{C}$ showed that an increase of 2°C only could be responsible for an enhancement of the rate of O_2 -absorption with $\pm 20\%$, far too low to account for the observed light effect. From these measurements another interesting result was obtained: the dark and the irradiated system have almost the same activation energy (46 ± 2 and 42 ± 2 kJ/mol). Clearly the irradiation did not change the activation energy of the rate determining step but merely augmented the number of catalytically active molecules.

This last argument may be very important, because it is known that in a basic reaction mixture most of the phthalocyanine molecules are present as dimers or dioxygen adducts⁵. On the other hand, only monomers are believed to be reactive⁴ in the catalytic reaction. Experiments at CoTSP concentrations between $1.0 \cdot 10^{-5}$ and $1.0 \cdot 10^{-4}$ M affirmed this view: at higher dimer/monomer ratios also an increase of the light effect was found. In a system without dimers (created by addition of 150 mg polyethyleneimine to a solution with 0.05 μmol CoTSP and 1 ml RSH but without NaOH) an O_2 -absorption of 126 mol O_2 (mol cat.) $^{-1}\text{s}^{-1}$ was found, and irradiation resulted only in a slight increase to 139 mol O_2 (mol cat.) $^{-1}\text{s}^{-1}$, which might be attributed to a slight elevation of the temperature. Addition of 6 mmol NaOH caused a dramatic change: due to disruption of the polymer-CoTSP bonds and formation of dimers a reactivity of 16 mol O_2 (mol cat.) $^{-1}\text{s}^{-1}$ was measured in the dark, while irradiation resulted in an increase to 66 mol O_2 (mol cat.) $^{-1}\text{s}^{-1}$. A further confirmation was found with experiments at different pH values. It is known⁵ that at pH = 7 CoTSP is present as monomers, whereas at higher pH values the equilibrium is shifted in favour of dimers. In agreement with this, almost no influence of the light on the rate was measured at pH = 7, while a threefold increase was observed at pH = 9.5.

Measurements with filters between the light source and the reactor showed that only light with a wavelength between 600 and 700 nm was active; this corresponds exactly with the position of a very strong band in the VIS-spectrum of CoTSP, attributed to a $\pi \rightarrow \pi^*$ transition¹. It may therefore be suggested that aggregation between phthalocyanine molecules in solution results from the interaction between the π -orbitals of the macro-cycles.

To determine the quantum yield a monochromatic light source (the 647.1 nm line of a Kr^+ laser) was used. Because the irradiation into our Warburg apparatus was not very efficient the measurement of the light intensity within the reactor with a $\text{Cr}(\text{urea})_6\text{Cl}_3$ solution as an actinometer⁶ was necessary. In this way a value of approximately 0.2 for the quantum efficiency has been measured.

In conclusion, we have found that absorption of light by CoTSP enhances the catalytic activity for the oxidation of RSH to RSSR. This enhancement can be ascribed to an increase of catalytically active monomers of CoTSP, caused by a light-induced shift of the dimer-monomer equilibrium.

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