Photolysis of Naphthol Green B in Aqueous Solution. Photoreduction of Fe(III) Induced by Ligand-to-Metal Charge Transfer Excitation

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The intense long-wavelength absorption of Naphthol Green B at $\lambda_{max} = 712$ nm is assigned to a ligand-to-metal charge transfer (MLCT) transition. LMCT excitation of the complex in aqueous solution leads to the reduction of Fe(III) to Fe(II) with a quantum yield of $\phi = 1.14 \times 10^{-3}$ at $\lambda_{irr} = 577$ nm.

Key words: Photochemistry, Charge Transfer, Iron
                Complexes, Naphthol Green B

Introduction

Naphthol Green B (or e.g. Naphthol Green, Acid Green 1, C.I. 10020) (NGB), an important commercial dye [1] is a pseudooctahedral Fe(III) complex which contains 1-nitroso-2-naphthol-6-sulfonate (NNSH) in the deprotonated state (NNS^-) as a bidentate ligand
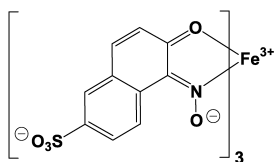
Although light-fastness is a significant property of dyes in general, the photochemistry of NGB has apparently not yet been examined. As an iron(III) compound it might undergo a photoredox reaction in analogy to numerous other Fe(III) complexes [2 – 4]. In the present study we explored this possibility. Owing to the water solubility of NGB this investigation was performed in aqueous solution.

Experimental Section

Materials

The water used for the measurements was triply destilled. Naphthol Green B was commercially available (Aldrich) and used without further purification.

Instrumentation

Absorption spectra were measured with a Varian Cary 50 or a Kontron Uvikon 860 spectrophotometer. The light source used for irradiation was an Osram HBO 200 W/2 or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Monochromatic light was obtained using Schott PIL/IL interference filters or a Schoeffel GM/1 high-intensity monochromator (band width 23 nm) with additional Schott cutoff filters to avoid short-wavelength and second order irradiation. In all cases the light beam was focused on a thermostated photolysis cell by a quartz lens.

Photolyses

The photolyses were carried out in aqueous solution in 1 cm spectrophotometer cells at room temperature under argon. Progress of the photolyses was monitored by UV-visible spectrophotometry. For quantum yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer, which was calibrated by ferrioxalate actinometry and equipped with an RkP-345 detector.

Results

Commercial NGB is supplied as a product which contains approximately 50% of the pure dye. In acidic solution NGB is not stable. Under these conditions the green colour disappears. The ligand NNS^- is protonated and released from the complex. NNSH shows its longest-wavelength absorption at $\lambda_{max} = 367$ nm ($\varepsilon = 4700$ M^{-1} cm^{-1}) [5]. Iron can then be analyzed spectrophotometrically by monitoring the complexes which absorb in the visible spectral region. Fe(III) is determined as red thiocyanato complex ($\lambda_{max} = 448$ nm, $\varepsilon = 4700$) [6]. As expected, NGB does not contain any Fe(II) which can be identified as $[Fe(o\text{-phen})_3]^{2+}$ with o-phen = *ortho*-phenanthroline ($\lambda_{max} = 510$ nm, $\varepsilon = 11500$) [7]. On the basis of the Fe(III) analysis the
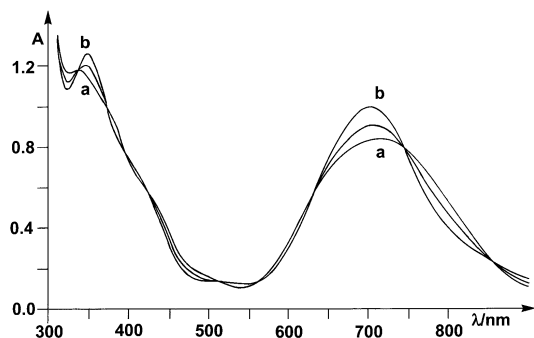
Fig. 1. Spectral changes during the photolysis of 3.92×10^{-5} M Naphthol Green B in H_2O under argon at r.t. after 0 min (a), 30 and 60 min (b) irradiation times with $\lambda_{irr} > 500$ nm (Hanovia 977 B-1 Xe/Hg 1 kW lamp and Schott cutoff OG 515/2), 1-cm cell.

commercial product was found to contain 54.2% of the pure dye.

The electronic spectrum of commercial NGB in water (Fig. 1) shows absorptions at $\lambda_{max} = 714$ nm ($\varepsilon = 21300$ M^{-1} cm^{-1}), 500 (sh, 4000), 420 (sh, 15200), 381 (sh, 23800) and 341 (29600). The extinction coefficients are determined on the basis of the Fe(III) content. Solutions of NGB are rather stable thermally, but light sensitive. Upon irradiation ($\lambda_{irr} > 520$ nm) a photoreaction takes place as indicated by the concomitant spectral changes (Fig. 1). Clear isosbestic points at 855, 744, 630, 564, 512, 428, 395, 378, and 339 nm are preserved over extended irradiation times. Since the photoproduct has an absorption spectrum which resembles that of NGB, the photolysis cannot be driven very far owing to inner filter effects. The photoproduct is apparently an Fe(II) complex of NNS as indicated by the presence of Fe(II) in the photolyzed solution. This conclusion is supported by the observation that the absorption spectrum of a Fe(II)-NNS complex has been reported to show a band at $\lambda_{max} = 708$ nm [5] which is close to the absorption maximum of the photolyzed solution. Moreover, the spectrum of NGB is largely recovered by exposing the photolyzed solution to air for a longer time. Fe(II) is thus apparently reoxidized to Fe(III). The quantum yield for the photoreduction of Fe(III) to Fe(II) is $\phi = 1.4 \times 10^{-3}$ at $\lambda_{irr} = 577$ nm).

Discussion

1-Nitroso-2-naphthol (NNH) and its derivatives may exist in two tautomers, the nitroso and the oxime form [8].
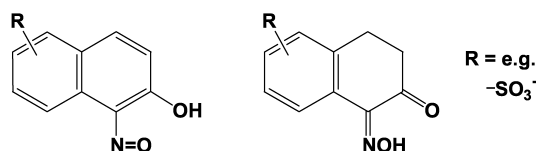
NNH coordinates in the deprotonated state (NN^-) as a monoanionic bidentate ligand. The coordinated anion can be referred to as an oximate or a phenolate. In both resonance forms the ligand may serve as charge transfer (CT) donor and acceptor. Nitroso groups provide acceptor functions [9], while phenolates are strong donors [10]. The oximate may also be viewed as a substituted ortho-quinone. Quinones are well known CT acceptors [11], but oximates have also donor properties [12].

NNH and its sulfonic acids show a longest-wavelength absorption at approximately $\lambda_{max} = 370$ nm [5, 13]. In the deprotonated state this band undergoes a red shift to about 420 nm. This absorption is apparently preserved as intraligand (IL) band in the coordinated state and appears as longest-wavelength absorption in complexes of redox-inert metals such as Zn^{2+} and Cd^{2+} [13]. In contrast, NN complexes of redox-active metal ions are intensely coloured [5, 13]. We suggest that these colours are caused by ligand-to-metal charge transfer (LMCT) absorptions of complexes with oxidizing metals and by metal-to-ligand charge transfer (MLCT) absorptions of complexes with reducing metals. Accordingly, the strong long-wavelength absorption of the $Fe^{III}NNS$ complex (NGB) at 714 nm is attributed to a LMCT transition while the long-wavelength band of the $Fe^{II}NNS$ complex at 708 nm [5] is assigned to a MLCT transition. It is certainly accidental that the LMCT and MLCT bands of both complexes are so close in energy. NNS complexes of other redox-active metals display such CT bands at quite different wavelengths [5]. This applies also to iron complexes with other ligands. For example, the MLCT band of $[Fe^{II}bipy_3]^{2+}$ (bipy = 2,2'-bipyridyl) appears at $\lambda_{max} = 520$ nm while the MLCT band of $[Fe^{III}bipy_3]^{3+}$ shows up at $\lambda_{max} = 614$ nm [10]. As ferroin this system is used as a redox indicator which changes its colour from red to blue upon oxidation of Fe(II) to Fe(III).

In aqueous solution, NGB is light sensitive. LMCT excitation ($\lambda_{irr} > 520$ nm) leads to the reduction of Fe(III) to Fe(II) in analogy to numerous other Fe(III) complexes [2–4]. The oxidation product of NGB is unknown, but the ligand itself may serve as electron

donor. This assumption is supported by the observation that the reoxidation of the photoproduct by O_2 does not completely recover the original concentration of NGB.

The quantum yield for the photolysis of NGB is relatively small. An efficient radiationless deactivation of the LMCT state to the ground state as well as a facile cage recombination of the primary radical pair (Fe^{2+}/NNS radical) may contribute to this. However, the bidentate coordination of NNS does certainly not facilitate a cage escape.

In conclusion, NGB in aqueous solution is light-sensitive but it appears to be almost light-fast. This phenomenon is caused by three effects. The quantum yield of the photolysis is rather low. The absorption spectra and hence the colours of NGB and its photolysis product are quite similar. Finally, owing to the similarity of the absorption spectra a strong inner-filter effect by the photoproduct prevents an extensive photolysis.

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