# Photofading Reaction of Bis[1-(4-dimethylaminophenyl)-2-phenylethanedithione]nickel(0) in the Presence of *N,N'*-Dimethylformamide

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**Synopsis.** Bis[1-(4-dimethylaminophenyl)-2-phenylethanedithione]nickel(0) was found to undergo photofading in the presence of dimethylformamide, by the action of photogenerated superoxide. Addition of a detergent suppressed the formation of superoxide, with an efficiency paralleling the fatty acid chain length.

We previously found that bis[1-(4-dimethylaminophenyl)-2-phenylethanedithione]nickel(0) (BDN), a Q-switch dye for neodimium laser was bleached in the presence of peroxide compounds[1] presumably via oxidation of BDN by peroxide. This bleaching was inhibited by inclusion of BDN into β-cyclodextrin.[1] BDN was also faded under darkness in the presence of *N,N'*-dimethylformamide (DMF).[2] In this case, BDN was reduced to its anion radical and the fading was not inhibited by inclusion into cyclodextrin but rather promoted in its presence.[3]

In addition we found that the reductive fading of BDN was promoted by illumination in the presence of DMF, and the mechanism of this reaction is the subject of the present work. Photo-generation of superoxide was expected to be the main cause as in the photofading of other dyes.[4,5] The authors incidentally found that singlet oxygen generation was inhibited by addition of a detergent in a Methylene Blue aqueous solution.[6] In view of this, the effect of detergents was also examined in the present BDN–DMF system.

## Experimental

BDN was purchased from Kodak Co., and DMF, toluene, adrenalin, sodium dodecyl sulfate (SDS), sodium octyl sulfate (SOS), and sodium hexadecyl sulfate (SCS) were obtained from Nakarai Chemical Co.

Electronic spectra were measured with a Shimadzu spectrophotometer MPS-5000. The photochemical reaction system was illuminated with an Ushio high-pressure mercury lamp Model 500 equipped with a Toshiba VY-50 filter.

The photofading rate was estimated by the photodecoloration ratio, *r*, defined by

$$r = \frac{OD^0 - OD}{OD^0} \quad (1)$$

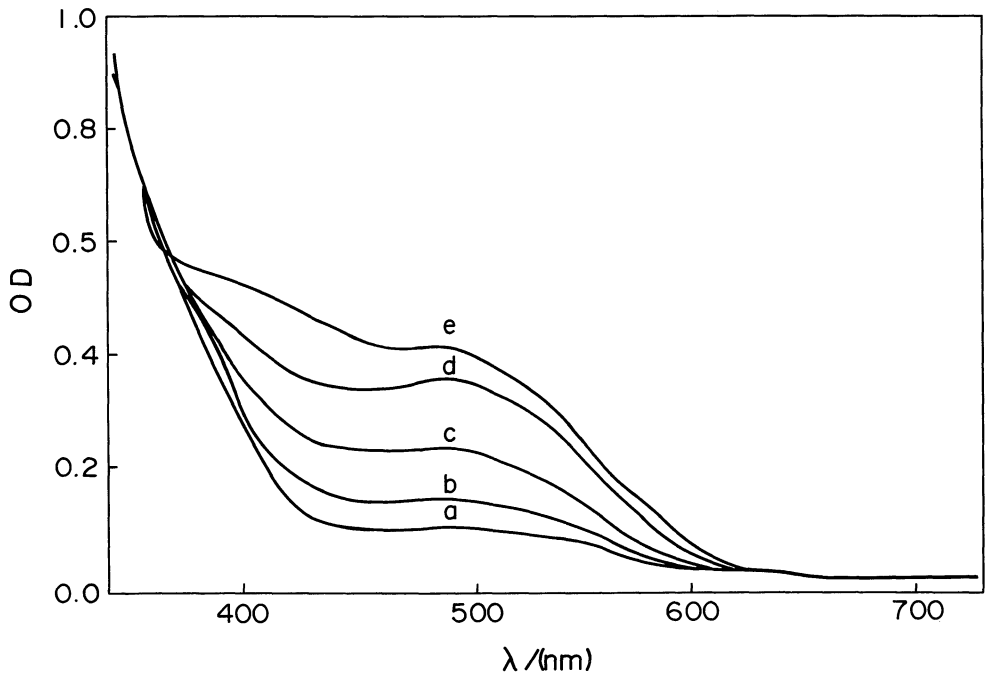


Fig. 1. Photooxidation of adrenalin to adrenochrome. [DMF]=5 mol dm$^{-3}$, [BDN]=$10^{-5}$ mol dm$^{-3}$, [Adrenalin]=50 mmol dm$^{-3}$, $I$=69.4 mW cm$^{-2}$. a: 0 min, b: 15 min, c: 30 min, d: 45 min, e: 60 min.

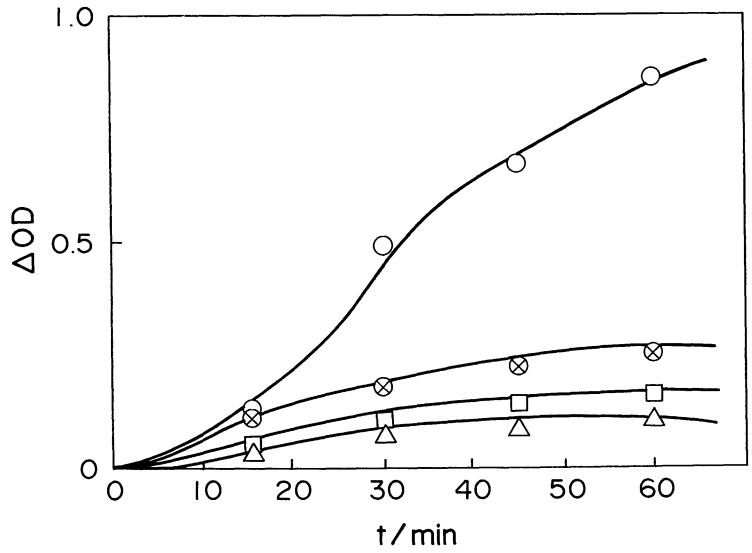


Fig. 2. Effect of detergents on the oxidation rate of adrenalin to adrenochrome. —○—: BDN alone, —⊗—: sodium octyl sulfate, $10^{-2}$ mol $dm^{-3}$, —□—: sodium dodecyl sulfate, $10^{-2}$ mol $dm^{-3}$, —△—: sodium hexadecyl sulfate, $10^{-2}$ mol $dm^{-3}$.

where, $OD^0$ and OD are the optical density at 1100 nm before illumination and that after $t$-min illumination, respectively.

## Results and Discussion

In darkness BDN fades in DMF via the formation of its anion radical. Illumination in DMF accelerated this reaction yielding the same product, BDNH, as in the fading in darkness. This was ensured by observing a common $R_f$ value (0.79) of the product by alumina thin layer chromatography (TLC), with DMF : toluene : methanol=1 : 0.75 : 1 as developer.

The generation of superoxide in this reaction system was suggested by the oxidative conversion of adrenalin to adrenochrom exihibiting an absorbance maximum at 490 nm (Fig. 1).[7] The following result also indicates the existence of superoxide. The photodecoloration ratio ($r$) of BDN in a DMF–water system ([DMF]=5 mol $dm^{-3}$) was 0.065 at 10-min illumination. The value of $r$ was 0.000 in the presence of 75000 units superoxide dismutase, which is a good quencher of superoxide.

It was found that $r$ of BDN was proportional to both the DMF concentration and the light intensity.

The maximum wavelength in the action spectrum of the BDN photofading was estimated to be about 300 nm, through experiments with a series of cutoff filters.

As in other photolysis systems[4,5] the following reaction sequence appears to hold for the present system.

$$\mathrm{BDN} \xrightarrow{h\nu} {}^1\mathrm{BDN} \quad (2)$$

$${}^1\mathrm{BDN} \longrightarrow {}^3\mathrm{BDN} \quad (3)$$

$${}^3\mathrm{BDN} + \text{solvent} \longrightarrow \mathrm{BDN}^+\cdot + \text{e(solvent)} \quad (4)$$

$$\mathrm{BDN}^+\cdot + \text{e(solvent)} \longrightarrow \mathrm{BDN}\cdot + \text{solvent} \quad (5)$$

$$2\mathrm{BDN}\cdot + \mathrm{H_2O} \longrightarrow \mathrm{BDNH} + \mathrm{BDN}^+\cdot + \mathrm{OH}^- \quad (6)$$

$$\text{e(solvent)} + \mathrm{O_2} \longrightarrow \mathrm{O_2}^-\cdot + \text{solvent} \quad (7)$$

This scheme is supported by the identifying BDNH as a final product by TLC. This compound may be an anion radical of BDN.

To estimate the rate of superoxide penetration through the micellar layer of a detergent, as in the case of singlet oxygen in Methylene Blue–detergent system, the effect of detergents to the BDN system on the oxidation of adrenalin to adrenochrome was investigated in the presence of a small amount of DMF. As seen in Fig. 2, the rate of adrenalin oxidation is in order SOS>SDS>SCS. Probably superoxide is generated in the center of micelles containing BDN molecules, and the triplet ground state oxygen is supplied sufficiently through the micelle membrane. The generated superoxide penetrates through the micelle membrane but it may disappear partly in the course of this penetration. When the micellein membrane is thicker, namely the fatty acid chain of detergent is longer, the disappearing fraction of superoxide is larger and hence the oxidative adrenalin-to-adrenochrome conversion is less efficient. The results in Fig. 2 are in line with this speculation.

## References

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